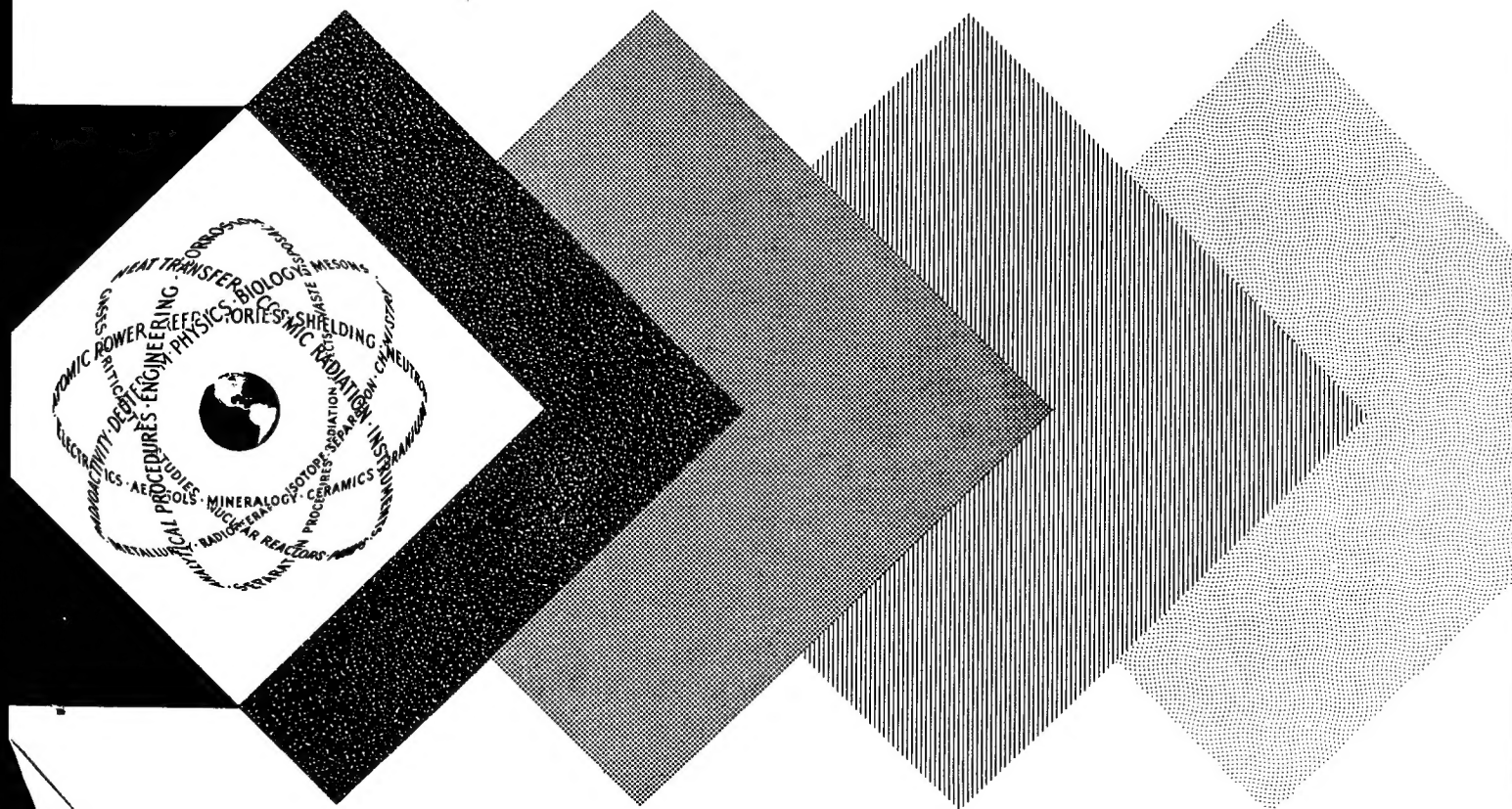# SOME EXPERIMENTS ON ELECTRICAL CONDUCTION IN VACUUM

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December 1957

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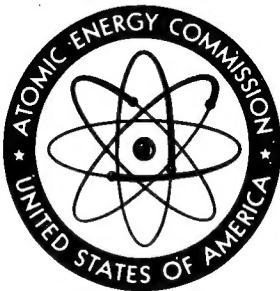
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SOME EXPERIMENTS ON ELECTRICAL CONDUCTION IN VACUUM

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December, 1957

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ABSTRACT

The conduction of electricity through a vacuum has been investigated in high voltage generators using beta emitters as current sources. The voltage attained by the generators was limited by vacuum conduction to values of tens to a few hundreds of kilovolts. The leakage current responsible for this limitation in most cases was found to consist of an exchange of charged particles between the two electrodes. The adsorption of contaminants on electrode surfaces was found to decrease the voltage at which appreciable vacuum conduction began to occur. In the systems studied, less than a monolayer of a slightly volatile material adsorbed on the anode surface had a marked effect. The nature of the positive particles was investigated by a mass spectrometric technique, and the secondary production coefficients involved in the exchange were studied.

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I -- CURRENT, VOLTAGE, AND FIELD
RELATIONSHIPS

The conduction of electricity through liquids, especially electrolytic solutions, and through gases and solids has been the object of many investigations. The conduction of electricity through a vacuum has received much less attention (except in the special case of thermionic currents in vacuum tubes). If a potential difference should be established between two absolutely clean metal electrodes in a perfect vacuum, few mechanisms for the passage of a current would seem to be available. At room temperature the Richardson-Schottky equation may be used to calculate the electron-emission current from the cathode at low fields,[1] and it is found that appreciable currents are drawn only at fields in excess of about 10^5 volts/cm. In actual practice, however, the electrodes are not absolutely clean, the vacuum is less than perfect, and consequently, measurable currents flow at potentials of several kilovolts. This effect has been recognized for many years by experimenters concerned with high voltages in vacuum and some tentative explanations have been offered.[2] This report describes some further investigations of the phenomena by which electric currents flow between electrodes in vacuum.

In discussing vacuum conduction we wish to exclude conduction in low-pressure arc discharges. We shall say that conduction is occurring in vacuum only if the pressure is sufficiently low so that an ion or electron traversing the gap has almost no chance of collision with a gas molecule. Since cross sections for such collisions are generally of the order of 10^{-15} cm^2 or less, the probability of collision in a 5-cm path is no more than about 0.02 for pressures less than 10^{-4} mm of mercury. Our experience has been that the vacuum

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conduction is unaffected by the presence of noncondensable gases at pressures below a few times 10^{-4} mm of mercury, and the experiments to be described were made at considerably lower pressures, usually less than 10^{-5} mm.

The high potentials used in our experiments are generated in place by the charging action[3] of beta rays emitted from radioactive sources (usually a $Sr^{90}-Y^{90}$ mixture). The isolated electrode containing the source is thus always the positive electrode (anode), and the negative electrode (cathode) always surrounds the anode, usually in a spherical or cylindrical geometrical arrangement. Although this arrangement limits the method to some extent, it has definite advantages. The current source is absolutely reliable, and it is very small, permitting freedom of choice in electrode shapes. The system can be very clean and is free of moving parts and without external electrical connections.

Our typical sources gave useful charging currents of the order of 50 μμa. (A one millicurie beta source emits a total current of 5.92 μμa.) These studies are concerned, therefore, with the low-current region, which is probably an advantage for the elucidation of fundamental current-carrying mechanisms. More-over, a typical system has a capacitance of the order of 1 μμf, so that at 100 kv the stored charge is only 10^{-7} coulomb, and the stored energy is only 0.01 joule. (For orientation it may be noted that if this energy were used to vaporize adsorbed gas, $\triangle H \approx 20,000$ cal/mole, the resulting pressure in a 1-liter flask would be 2×10^{-3} mm.)

EXPERIMENTAL METHODS

Apparatus

Figure 1 illustrates one of the basic experimental arrangements. The charging current of electrons comes from a beta source in the anode, a, and traverses the vacuum space to arrive at the cathode, c. The anode (shown enlarged on the figure) contains the beta source, b, and is supported on a fused quartz rod, q, 3 mm in diameter. Alpha particles (used for voltage measurement) from a polonium source, p, on the anode reach a flow proportional counter, f,
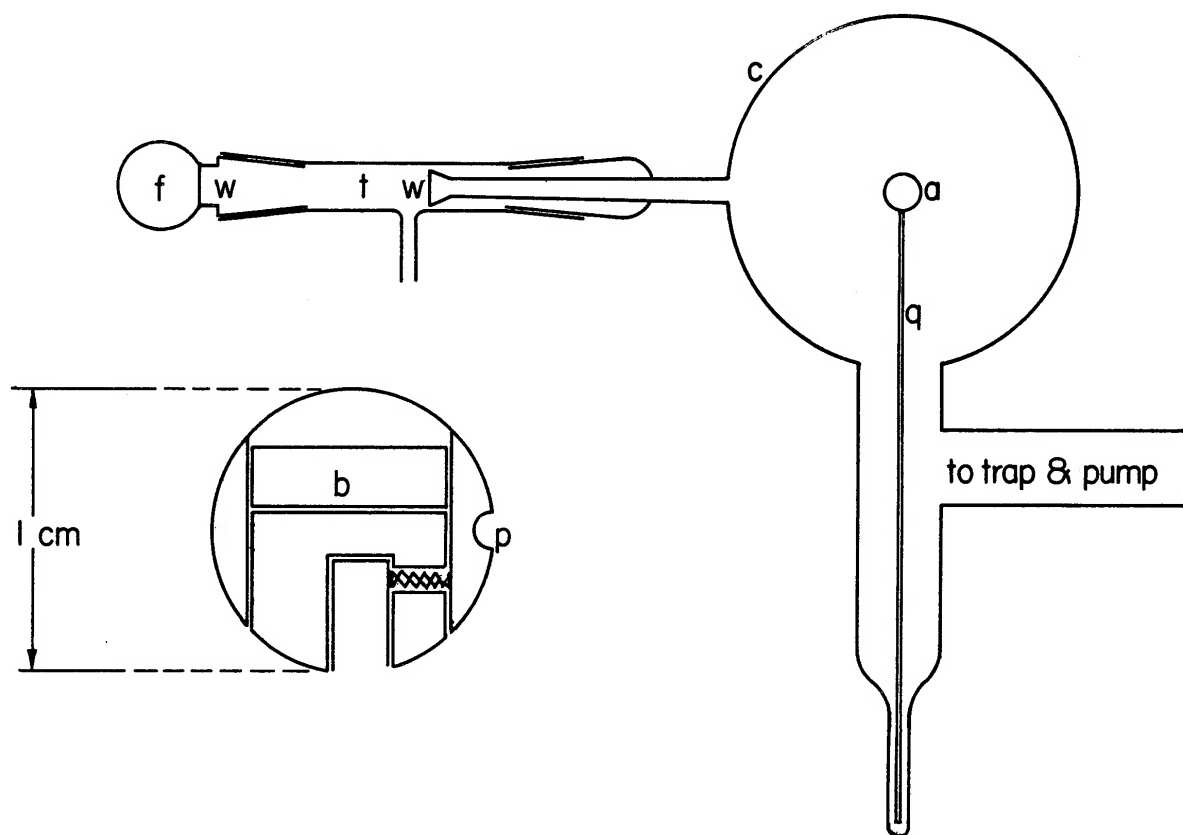
Fig. 1.   Typical Experimental Arrangement.   Enlarged Section of Anode at Lower Left.

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after passing through two thin mica windows, w, and an intervening absorption tube, t. This apparatus was made from a 1-liter round-bottom Pyrex flask; there were no grease joints or gaskets of any kind in the high vacuum part of the system. (The mica window was sealed with Corning 7570 glass to soft glass which, in turn, was graded to Pyrex in the usual way.) The system was evacuated by a mercury diffusion pump and trapped with a Dry Ice--acetone mixture. Pressures were measured by either an ionization gauge or a McLeod gauge, the latter placed between the trap and the diffusion pump.

For some experiments a similar, but larger, apparatus was used, which was constructed from a 22-liter Pyrex flask. Two other systems had cylindrical rather than spherical Pyrex cathodes, sometimes with a cylindrical anode. The largest apparatus used a cylindrical tank of tinned brass, 63 cm long by 35 cm in diameter, as the cathode. The end plates were sealed with neoprene O-rings. The tank was evacuated by an oil diffusion pump using Octoil-S or DC-703 silicone oil and was trapped by only a water-cooled baffle plate.

Systems with cylindrical cathodes usually had one or two cylindrical grid structures near the cathode wall. The large brass system had one grid of coarse wire mesh 3.5 cm from the cathode (grid 1) and one grid of 0.005-in. nichrome wires spaced 0.6 cm apart, 5.1 cm from the cathode (grid 2). Such grids were sometimes divided electrically, and external connections were provided through metal-to-glass seals.

A typical anode is shown in Fig. 1. Spheres of other diameters and, rarely, cylinders with hemispherical ends were also used. Although there were some variations in details of construction, all contained the same beta sources beneath a smooth-fitting spherical cap about 0.002 in. thick. Anodes were of aluminum unless otherwise stated. The connection between quartz rod and anode had to be secured with spring-loading or with screw threads, or some other device, because the electrostatic forces were often sufficiently strong and asymmetric to pull the anode off the rod.

Voltage Measurement

Each vacuum chamber was equipped with a thin (approximately 2 mg/cm^2) mica window which led to an absorption tube, the opposite end of which was connected through another mica window to a flow counter. An alpha source (Po^{210}) was so mounted in a recess in the anode that the counter could "see" it through the two windows. The pressure in the absorption tube could be varied between 0 and 1 atm., so that the range of the alpha particles could be measured. The potential difference between the anode and the counter (which was at ground) was determined by comparing the extrapolated range of the alpha particles at the unknown voltage with the extrapolated range when the anode was grounded. The well-known range--energy relation[4] was used to convert this range difference to alpha-energy increase. This alpha-particle voltmeter had a routine accuracy of $\pm$ 5 kv.

In preliminary experiments the electrostatic attraction of the anode for a grounded metal disc mounted flush with the cathode was used as a measure of the voltage;[5] later comparison with the alpha-range determinations indicated that uncertainties in the shape of the field near the disc led to large errors.

A very convenient method for routine measurement of the anode voltage was developed, based on the reduction in beta-ray intensity at the cathode, when the anode came to such high positive potential that many beta particles were returned to the anode by electrostatic attraction. An ionization chamber connected to a simple dc amplifier was placed outside the glass flask, or at a thin window in the cathode wall. The ion-chamber current was calibrated for each system as a function of anode voltage determined by the alpha-particle method. At 300 kv, for example, the beta intensity might be about half that at zero voltage.

In some experiments, to be described in a later paper, positive ions emitted by the anode were investigated by magnetic and electrostatic deflection. The magnitude of the electrostatic deflection is, of course, inversely proportional to the energy of the ions per unit charge. Anode potentials calculated from electrostatic deflections agreed with the values obtained from alpha-range measurements.

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Current Measurement

It was often necessary to measure currents in the $\mu\mu a$ range--e.g., beta-ray charging currents, leakage currents to cathode grids, and beta-ray ionization chamber currents. This was done by measurement of the voltage drop across a resistor of appropriate size (10^9 to 10^{12} ohms) with a vacuum-tube electrometer. Grid currents at high bias voltages could be measured accurately only when the systems were protected by "dc shielding"; i.e., all insulators touching the sensitive leads were in contact only with conductors at the same potential. In one apparatus, automatic recording was provided for the various grid and ion-chamber currents. For the measurement of beta charging currents, the particular source--anode combination was placed in one of the vacuum chambers and connected to the micromicroammeter; the electron current drawn from ground after the system had been evacuated was taken as the charging current (at zero anode potential). Variation of this current with application of positive or negative biases of a few volts did not amount to more than a few percent.

Preparation of Sources

Most of the beta-ray sources consisted of an equilibrium mixture of the 25-yr fission product Sr^{90} and its daughter, 64-hr Y^{90}. (In a few early experiments, 54-day Sr^{89} was used.) In the usual procedure, the Sr-Y mixture, obtained through the Isotopes Division of the Atomic Energy Commission, was concentrated by precipitation as the carbonate and then was dissolved in dilute nitric acid. The solution was evaporated to dryness on a 3/8-in.-diameter, 0.005-in.-thick stainless steel disc which had previously been soldered to a 0.025-in. galvanized iron disc. (The iron backing was provided to make possible remote magnetic handling of the completed sources.) After deposition of the radioactive material, the entire source was "canned" in nickel by thermal decomposition of nickel carbonyl. This process gave a vacuum-tight coating, ~ 0.001 in. thick, which served to isolate the active material and to prevent the spread of contamination. A series of these sources, from 2 mc to 100 mc, was prepared.
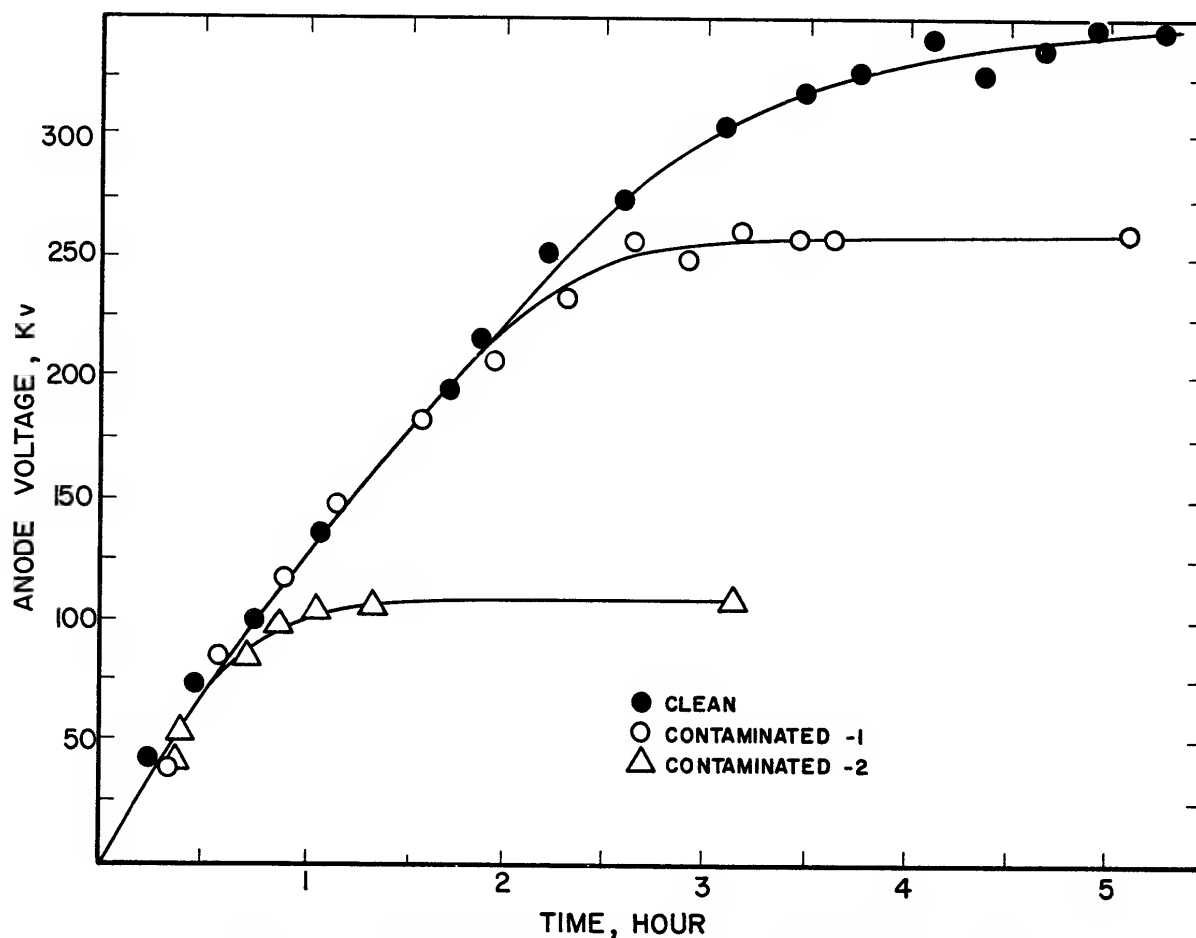
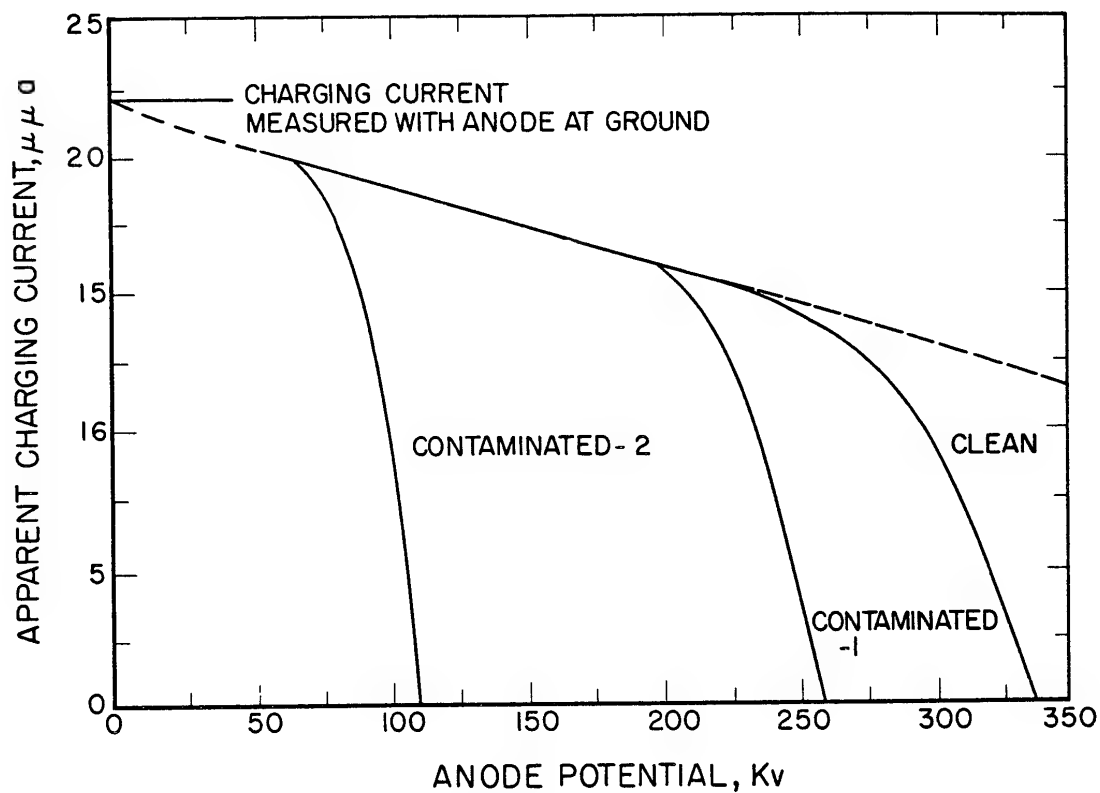Fig. 2.   Charging Curves for 22 μμa Source in Small Spherical System.

Fig. 3. Net Charging Current as a Function of Voltage.

The Po^{210} alpha-particle sources (for voltage measurements) were prepared
by hydrogen reduction onto palladium foils. Up to approximately 1 mc was
deposited on a few square millimeters of foil.

DISCUSSION OF RESULTS

Charging Rate

Figure 2 shows the anode voltage, after intentional grounding (by a Tesla
coil discharge), as a function of time for the glass system (Fig. 1) in three
different states of cleanliness, with a 22-$\mu\mu$a beta source. The time derivatives
of these curves are plotted in Fig. 3 to show the apparent or net charging
current as a function of anode potential. The upper line, which is extrapolated
to the right, represents the real beta charging current in the absence of any
backward current. A backward (leakage) current, which we call the dark current,
sets in at a particular voltage in each case and increases sharply with increasing
voltage. The dark current, as measured by the departure of the individual curves
from the upper line, is discussed in the following section.

Current--Voltage Relation

The dependence of the leakage current through the vacuum space on the anode
potential can be investigated by experiments with beta sources of various strengths.
The steady voltage achieved measures the anode potential at which the leakage
current just balances the charging current. Several series of such experiments
have been run, and two typical sets are summarized in Table I. The charging
currents for the three beta sources were measured at zero anode potential; a
correction was then applied for the electrostatic reduction in the beta-ray flux
reaching the cathode. From the data in Table I and from the charging curves in
Fig. 3, we show in Fig. 4, on a log-log plot, the vacuum dark current as a function
of anode voltage.

Clearly, the current is a steep function of the voltage, and the relationship
depends on the particular experimental conditions. In attempting to classify the

Table I. Voltage and Charging Current

	Charging current measured (μμa)	Charging current corrected (μμa)	Voltage attained (kv)
Series 1	4.0	3.8	27
	20	19	44
	72	66	63
Series 2	4.0	3.5	90
	20	16	111
	72	58	138

Table II. Voltage and Cathode Fields

System	Cathode radius (cm)	Limiting voltage (kv)	Cathode field* (v/cm)
Cylindrical metal, oil-	17.5	100	345
pumped, 1 cm-radius	7.5	90	1840
spherical anode	3.8	85	7940
Spherical glass, 0.5 cm-	17	91	164
radius anode, not clean	3.65	94	4100
Same as above, cleaner	17	136	240
	3.65	128	5600

*With a spherical anode in a cylindrical cathode, the cathode field is estimated for spherical geometry with the same radii. That this is a fair approximation to the actual field in the median plane (maximum cathode field) was shown by probe potential measurements in an electrolyte bath.
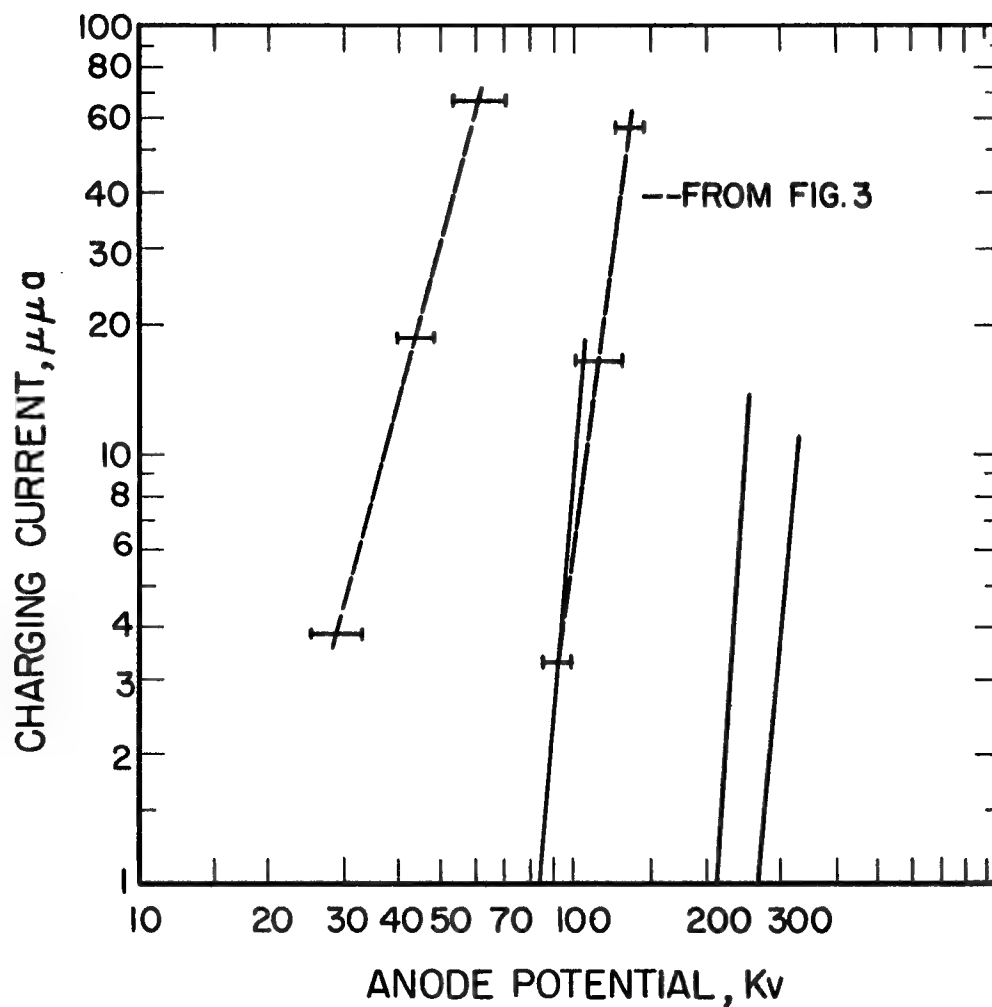
Fig. 4. Relation between Charging Current and Equilibrium
Voltage Attained (dotted lines). Leakage Current
as a Function of Voltage below Equilibrium (solid
lines).

various conditions, we have found it necessary to consider not only the anode
voltage, but also the geometrical arrangement, the potential gradients at the
electrodes, and the cleanliness of the system. Three broad classes of behavior
are considered in the next three sections.

A question that might be raised is whether the beta charging current
causes the leakage current by the production of appreciable numbers of secondary
electrons at the cathode. That this effect is not serious is shown by experi-
ments in which the cathode was irradiated by an additional beta source (not on
the anode). For example, a particular system gave 77 kv with a 4-μμa charging
current, and 73 kv with the same charging current and an additional beta flux
of 11 μμa striking the cathode.

In every system, we tested for the existence of a leakage current along the
quartz support rod by means of an electrical connection to its base. In the
very few instances in which an appreciable leakage current was observed, sub-
stitution of a clean rod corrected this. Several methods for cleaning the rods
were used, and any one that ended with prolonged rinsing in very pure water or
acetone was found to be satisfactory.

<div align="center">Cathode Emission</div>

As shown in the next section, at low cathode fields the voltage developed
is quite insensitive to variations in the electrostatic field at the cathode
surface. If the cathode field is increased to a value above 10 kv/cm, by re-
ducing the separation between electrodes or by using concentric cylindrical
rather than spherical electrodes,[6] it can be a decisive factor in the dark current.
In one series of ten experiments with cylindrical aluminum cathodes of various
radii, from 2.05 to 4.5 cm, and a 0.5-cm-radius cylindrical anode, the recorded
limiting voltages ranged from 25 to 130 kv, but the corresponding cathode fields
were always between 9 and 18 kv/cm. In this series the anode fields were from
37 to 126 kv/cm, a variation almost as great as the variation in total voltage.
Similar results were obtained in a series with stainless steel cathodes. Tests

with this apparatus, using 24 other cathodes of various materials (brass, gold, magnesium, glass, and plastic) and with various surface preparations (polished, rough, oxidized, electroplated, evaporated, evaporated and never exposed to air, and coated with such substances as "Dri-Film," fluorocarbons, aquadag, and paraffin) gave steady voltages between 40 and 130 kv, and in no case did the cathode field exceed 18 kv/cm. These leakage currents can hardly be field emission,[1] even if the work function should be as small as 1 ev and even making reasonable allowance for increase in field at local surface irregularities.[7]

In some experiments discussed in the next section we used cathode grids with sufficient negative bias to screen the cathode surface from the electrostatic field of the anode. In such cases the field is concentrated about each grid wire, the field there being roughly 100 times the cathode field in the absence of a grid. Only in these cases have we observed "cathode" fields much in excess of 15 kv/cm. For example, an all-glass system with a 0.5-cm-radius cylindrical anode and 3.6-cm-radius cylindrical cathode grid biased to -2000 v has given a steady potential of about 230 kv. Here, we estimate the field about the grid wires to be approximately 325 kv/cm. The leakage current of electrons drawn from this grid was approximately the same as the charging current. The effect of temperature on this leakage current was investigated. Comparison of the experimental current-voltage-temperature relationship with the predictions of the Richardson-Schottky equation[1] yields quite reasonable values of the important parameters, namely a work function of 2.4 ev and a local field intensification factor of 7.6.

Exchange Current

In typical systems, with spherical anodes of not more than a few centimeters in diameter, and without cathode grids, the steady voltages attained were limited by a leakage current qualitatively different from those just described. To summarize the results of a large number of trials, we may say that the "contaminated systems," oil-pumped or gasketed or not very clean, gave voltages of about 100 kv regardless of the cathode field (for fields below 10 kv/cm). Sample data are given in Table II.

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Clearly, the leakage current is determined by the total voltage, rather than by the cathode field.

Under similar conditions the voltage developed is somewhat dependent upon the anode surface field. For example, the average anode voltage for four trials with a 0.5-cm-radius anode in a 6.5-cm-radius fairly clean spherical glass system (22 μμa beta current) was 186 kv, with a corresponding anode field of 404 kv/cm. With a 1.25-cm-radius anode (20 μμa beta current), the same system gave an average of 265 kv, with a corresponding anode field of 262 kv/cm. It is interesting that the pertinent factor is the field over the whole anode: when a protruding rod with a 0.10-cm spherical radius at its end was added to the 0.5-cm-radius anode, the voltage attainable was not appreciably affected, although the local field must have been roughly five times that on the rest of the anode.

The behavior of these systems clearly resembles the phenomena termed "total voltage" breakdown by Trump and van de Graaff.[8] Although these workers apparently were referring to vacuum spark breakdown, the initial mechanism which they propose seems at least as applicable to the dark current leakage in our systems. In brief, and without mention of their reference to the possible role of photons, they proposed a self-sustaining chain mechanism, with positive ions crossing from anode to cathode, making there on impact secondary electrons which return to the anode and make additional positive ions. The difficulty with this hypothesis, as pointed out by the same group, is that each positive ion makes only about 10 secondary electrons, whereas about 1000 electrons are needed to make one positive ion at the anode.

The dark current which we observe is very similar to the "electron loading" in ion-accelerating tubes described by Turner.[9] Very informative experiments on "electron loading" have been briefly reported by McKibben and Boyer.[10] They suggest that not only electrons but also negative ions travel from cathode to anode, and that it is principally the negative ions which produce the secondary positive ions (mostly H^+) at the anode.

This "exchange mechanism" would be expected to produce a sudden onset of unlimited leakage current at that critical voltage at which the chain reaction

becomes divergent. This is approximately, but not exactly, the behavior shown in Fig. 3. To explain the small but real variation in voltage with current in Fig. 4 (and Turner's empirical[9] $I = \underline{k} \, \underline{V}^6$) it would be sufficient to introduce a slight dependence of the secondary ion coefficients on the current drawn. We propose to present, in a subsequent paper, evidence on the nature of the ions and the electrode processes.

The chain mechanism evidently makes use of impurities on the electrode surfaces. The small spherical system, with a 0.5-cm-radius anode in a 6.5-cm-radius Pyrex flask, gives about 100 kv when dirty, and about 250 kv when cleaned by ion bombardment in a low-pressure Tesla coil discharge. After repeated baking out under vacuum, the same system will reach about 400 kv.

If a wire grid structure outside the cathode surface is given a negative bias of the order of 1000 v, sufficient to cut off the entire cathode surface from the anode field, secondary electrons and negative ions (except the small fraction formed on the grid wires) cannot return to the anode. With the exchange chain broken in this way, the large (contaminated) metal system gives as much as 325 kv, as compared with about 80 kv without the grid. The new limitation at the higher voltage can be due to any of at least three causes, according to experimental conditions: (1) failure to maintain cathode cut-off because of inadequate grid bias, (2) field-induced electron emission from the grid, and (3) "spontaneous" emission of positive ions from the anode, as discussed in the next section.

One series of trials that illustrates limitation caused by the failure to maintain cathode cut-off used a 2-cm-radius anode in the large metal system, with two cathode grids. Grid 2 (the one farther from the cathode) carried the negative bias. Grid 1 was at a positive potential, to collect electrons (and negative ions) produced at the cathode. The electron current collected by grid 1, $\underline{I}_1$, remained very small as the anode charged up, until a critical value of the voltage $\underline{V}$

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was reached, at which I_1 suddenly increased to a large value (> 100 μμa), and

an exchange-dark-current limitation was in effect. The critical value of V was

shown to depend upon the grid 2 bias voltage; typical values of the critical

voltage were 100 kv at -600 v bias, 125 kv at -900 v, 150 kv at -1200 v, and

180 kv at -1500 v.

<center>Anode Emission</center>

When a 0.5-cm radius anode was used in the apparatus mentioned immediately

above, the behavior of I_1 as a function of V was very different. With any grid

2 bias value from -300 to -1800 v, the electron current collected on the positive

grid 1 was given, approximately, by $I_1 = k \, V^3$. This current consists of secondary

electrons produced at the cathode by positive ions from the anode. That it

increases continuously with anode voltage, V, shows that it is not an exchange

current, and the absence of any dependence on grid 2 voltage shows that the

cathode is completely cut off from participation in the generation of the positive

ions. The value of k, for I_1 in micromicroamperes and V in kilovolts, was

measured as 17.1 x 10^{-5} for a 180 μμa beta-ray charging current, as 10.1 x 10^{-5}

for a 50 μμa charging current, and as 5.4 x 10^{-5} for a 15 μμa charging current.

The variation with beta source strength suggests some role for the beta-particles

in the production of the positive ion emission. Values of I_1 up to > 1000 μμa

have been recorded reproducibly.

CONCLUSION

The dark currents encountered in this work may be grouped in three classes, according to their dependence on system parameters. At cathode fields greater than about 10 kv/cm, appreciable field-dependent currents were drawn from the cathode which were rather insensitive to other system parameters. At high anode fields, "spontaneous" positive ion currents were drawn from the anode which gave rise to a secondary electron current on striking the cathode. At lower anode and cathode fields, an exchange current was observed which was a very steep function of the total potential difference between the electrodes, and which was very sensitive to the cleanliness of the vacuum system.

II--EFFECT OF ADSORBATES ON ELECTRODES

In the previous section, evidence was presented to show that electrical currents can flow across vacuum spaces at relatively low electrode fields by means of an exchange mechanism in which positive particles from the anode strike the cathode, releasing secondary negative particles which in turn strike the anode, releasing additional positive particles, and so on. We observed that the voltage at which this current became important was strongly influenced by the cleanliness of the vacuum chamber. The experiments reported in this section were made in an effort to throw some light on the role contaminants play in electrical leakage across vacuum gaps.

EXPERIMENTS

All the experiments discussed here were performed in the 1-liter and 22-liter spherical glass chambers described earlier. Furnaces were constructed around both systems to provide temperature control above room temperature, and provision was made for immersing the 1-liter chamber in liquid nitrogen and other coolants.

Slightly volatile materials were applied to the anode of the 1-liter system (and incidentally probably to all other surfaces in the system) by loading a quantity of activated alumina with a layer of the desired material and allowing the anode surface (also aluminum oxide) to come to equilibrium with the loaded adsorbent in vacuum. The mechanics of this procedure were as follows:

The lower section of a container of the type shown in Fig. 5 was outgassed by flaming under vacuum and then opened to dry helium. Weighed amounts of freshly outgassed Alcoa Type-F-1 alumina (100-200 mg) and the adsorbate (3-50 mg) were next introduced into Sections a and b respectively, the container was again evacuated, and Part a and the alumina it contained were again
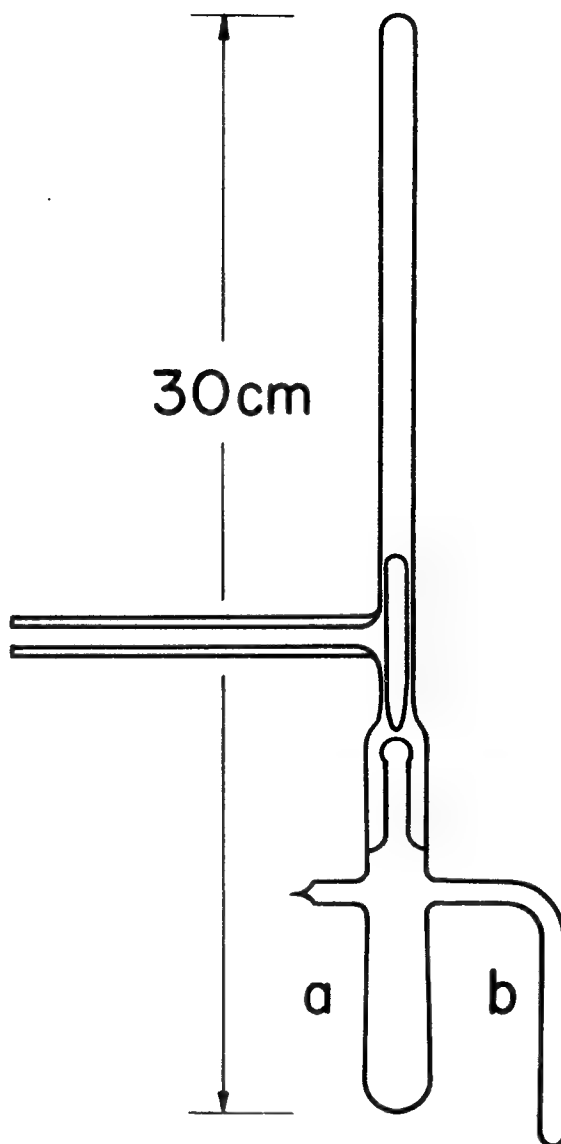
Fig. 5.   Contaminant Container

thoroughly flamed. Where practical, the substance in Part b was purified by warming it enough to make it evaporate and recondense higher in its tube. Then, with the entire assembly cool and at "stick" vacuum on the McLeod gauge, the container was sealed off at a constriction and removed to an oven, where it was left for ten to twelve hours at 100-150°C. In all cases where satisfactory adsorption was obtained and the amount of the adsorbate was less than the amount necessary for saturation, all the substance in Section b disappeared after the first hour or two at this temperature. The additional time was allowed so that equilibrium could be reached between all parts of the alumina surface.

When several of these containers were ready, they were sealed to a common manifold and the manifold was attached to the 1-liter chamber. The entire system was then evacuated by a mercury diffusion pump trapped with liquid nitrogen, and flamed thoroughly. The vacuum chamber was then sealed off from the pumps at a constriction provided for this purpose between flask and trap. Introduction of the volatile material into the main vacuum vessel was accomplished by breaking the thin-walled bulb to the desired container with the armature provided and then holding the armature up magnetically to leave the 5-mm-diameter opening unobstructed. After equilibrium had been established and the desired measurements made, the container was placed in liquid nitrogen (to provide temporary pumping) and sealed off near the middle of the heavy-walled tube leading to it. Then the entire procedure was repeated for each of the remaining containers.

The equilibration of anode and alumina, gauged by stabilization of the anode voltage, appeared in most cases to be complete within a few hours. Although the process was reversible, the approach to equilibrium appeared to be more rapid for adsorption than for desorption; hence, experiments were usually carried out by using the containers in order of increasing degree of saturation with a particular contaminant.

RESULTS

Adsorption Experiments

Data on the effect of contamination of the vacuum chamber were obtained
by the procedure outlined above. The results for a number of substances
are shown graphically in Fig. 6. The anode potential attainable with a 22-$\mu\mu$a
source and a 1-cm-diameter anode in the 1-liter system is plotted against the
amount of contaminant on the alumina, expressed in grams per square centimeter
of surface area. At least one of the experimental points for each contaminant
(with the exception of n-octadecanol) represents an amount of adsorbate in
excess of the saturation amount, i.e., some contaminant could still be seen on
the inside surface of the containing vessel after equilibration in an oven had
been carried out. With regard to distillation and diffusion processes, such
samples should be equivalent to a sample of the pure contaminant. For this
reason, distinct breaks are indicated in the curves of Fig. 6. All points
to the right of the breaks in their respective curves represent alumina samples
which were visibly more than saturated; points to the left of the breaks repre-
sent samples which were not. A straight line is drawn through the last few
points for unsaturated samples in each case, and its intersection with a hori-
zontal line drawn through the points for saturated samples is assumed to indi-
cate roughly the saturation amount of contaminant. The curves for sulfur and
for n-tetracosane, Run 1, show that this method of handling the data is
reasonable.

In Fig. 7 the data are again plotted, this time as a function of the
degree of saturation of the alumina. The amount of contaminant needed for
saturation has been assumed to be the amount corresponding to the breaks in
the curves of Fig. 6. Since no such point was available for n-octadecanol,
additional samples of this material with alumina were made up to confirm
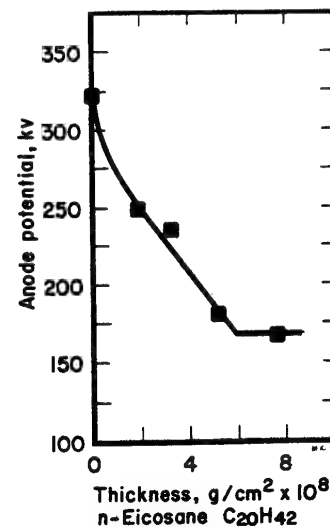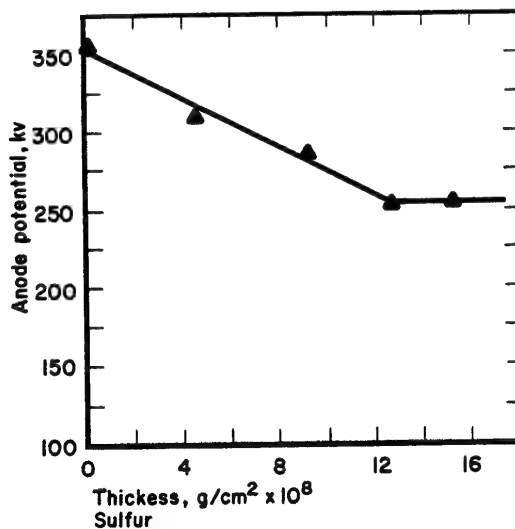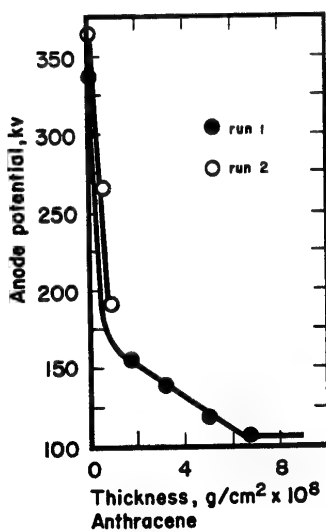visually that the saturation amount chosen was approximately correct.
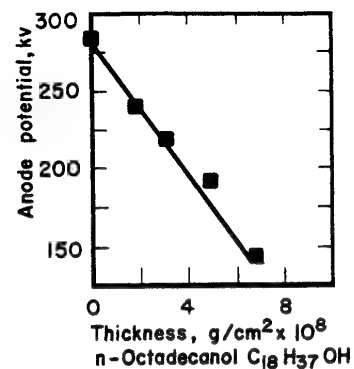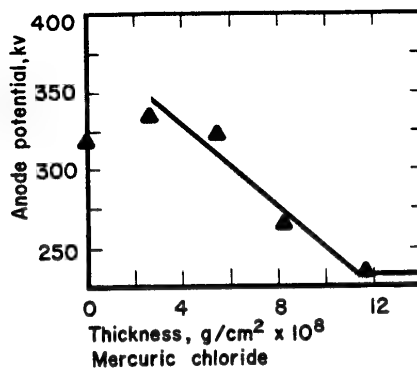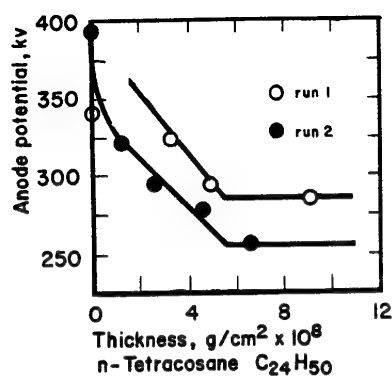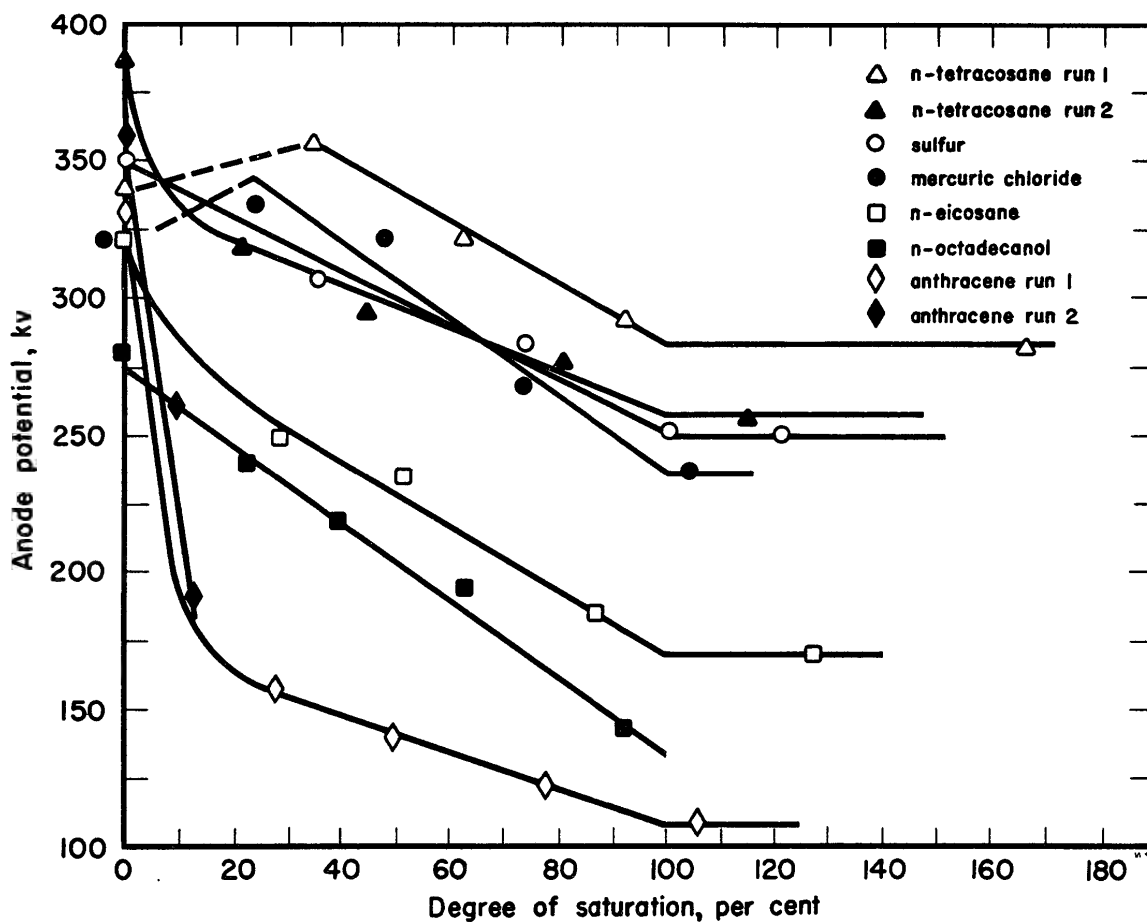
Fig. 6. Effect of Contamination

Fig. 7. Effect of Contamination

In both figures the zero-adsorption points for n-tetracosane, Run 1, and mercuric chloride fall off their respective curves. In both cases, no alumina was present in the chamber when the initial point was taken, and the first alumina samples probably removed some unknown contaminant from the system, thereby offsetting the effect of the contaminant being introduced. Another n-paraffin in addition to those shown, n-dotriacontane $(C_{32}H_{66})$, was tried as a contaminant in the presence of alumina. This proved to have such a low vapor pressure that no visible amount of distillation into the alumina occurred, and there was no diminution of anode potential (320 kv) as a result of the introduction of the sample into the system. Anthraquinone also, although it distilled into the alumina satisfactorily, caused no voltage reduction from a starting potential of 320 kv.

The specific surface area of the Alcoa Type-F-1 alumina used was assumed to be 240 m^2/g from the data of Stowe,[11] who measured the area by the Brunauer-Emmett-Teller method with nitrogen. This specific surface area can be taken as an approximate value in our case, although it may not be precisely applicable for two reasons. First, the specific area is known to vary from one batch to another. (All the alumina used in this work was taken from a single container.) Second, it is not necessarily true that all the surface area available to nitrogen in Stowe's experiments is available to the much larger molecules under discussion here. We measured adsorption isotherms of ethyl ether and ethyl bromide at room temperature on a sample of our alumina. Assuming that the packing of the molecules on the surface was similar to that in the liquid state,[12] we calculated specific surface areas of 270 and 320 m^2/g respectively for the ether and ethyl-bromide cases. Although the packing assumption may not be a good one, the results do indicate that the major portion of the surface area is available to these two molecules.

Alumina samples saturated with sulfur were used for two other experiments not included in Figs. 6 and 7. The final voltages were 225 and 257 kv. In

another experiment, with a sample saturated with n-tetracosane, the equi-
librium potential was 283 kv. These results confirm the indications of the
duplicate runs with n-tetracosane and anthracene, i.e., that the voltages attained
are reasonably reproducible.

Temperature Dependence

The effect of ambient temperature on the voltage attained in a thorough-
ly outgassed chamber is shown in Fig. 8 . Here, the equilibrium voltage is
plotted against the reciprocal of the absolute temperature for four different
experimental systems. It is noteworthy that all four arrangements showed
a temperature-sensitive and a temperature-insensitive region, and that,
although the data available are not sufficient to be conclusive, the voltage
attained in the temperature-sensitive region appears to be insensitive to
the geometry and source strength used.

The effect of having the two electrodes at different temperatures was
studied by cooling and heating the 1-liter chamber at a rate rapid enough for
the temperature of the anode to lag behind that of the cathode. (Heating
was at the rate of 1°/min. The cooling rate varied from 2°/min at 250°C
to 0.5°/min at 80°C.) The results obtained with a 1.1-cm-diameter anode and
a 94-$\mu\mu$a source are shown in Fig. 9 . Two separate curves were taken on
cooling, and the values obtained were quite reproducible. Only a single
curve was taken on heating. At two points in the experiment, indicated by
the arrows on the curves, spark breakdown occurred, but the system charged up
again to its new equilibrium value.

Since the anode was not in good thermal contact with its surroundings,
the temperatures shown in Fig. 9 are cathode temperatures. In order to esti-
mate the corresponding anode temperatures, the apparatus was run through a
similar heating and cooling cycle while under vacuum, with a fine thermo-
couple attached to the anode. The anode temperatures measured in this way
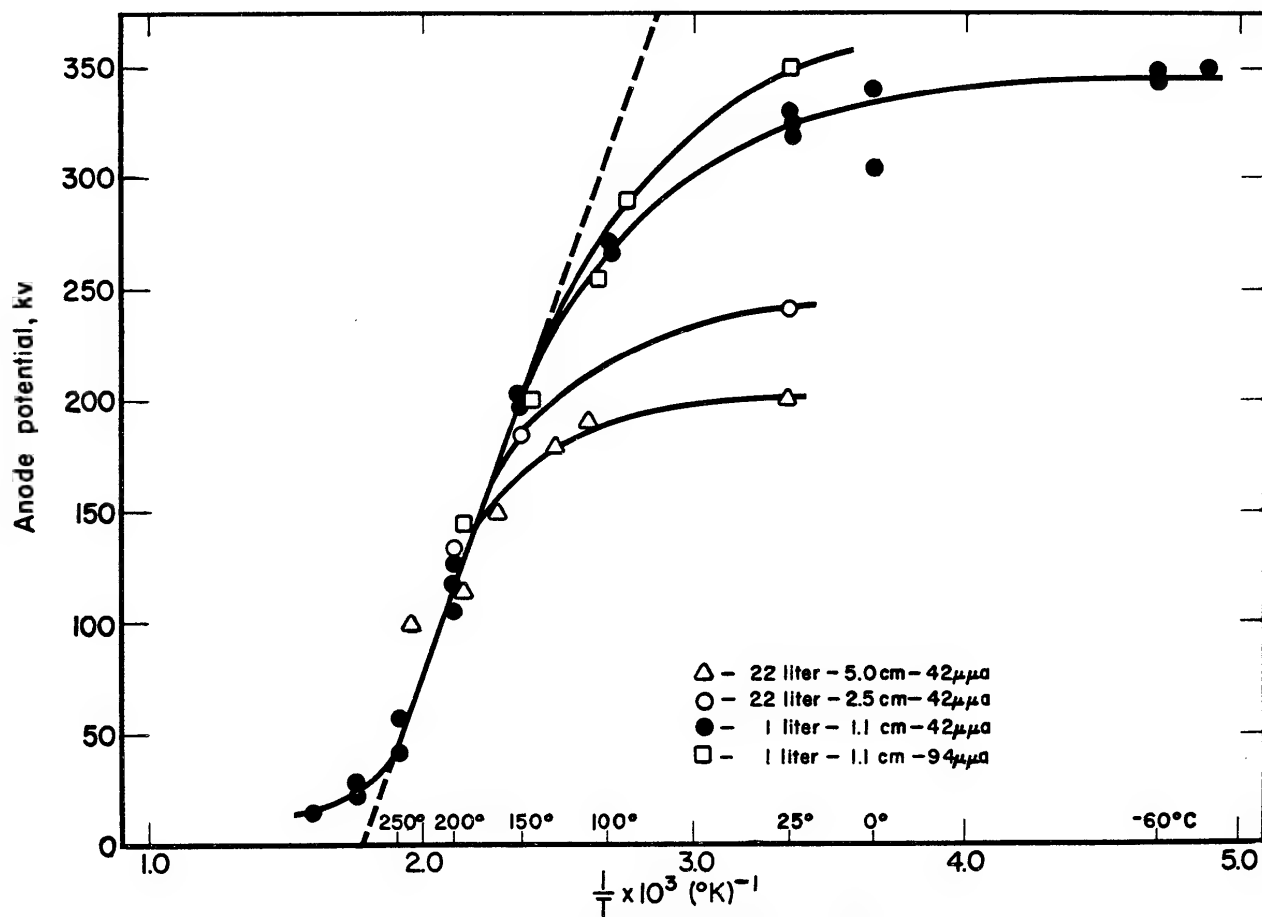were taken as minimum temperatures, since the thermocouple provided an
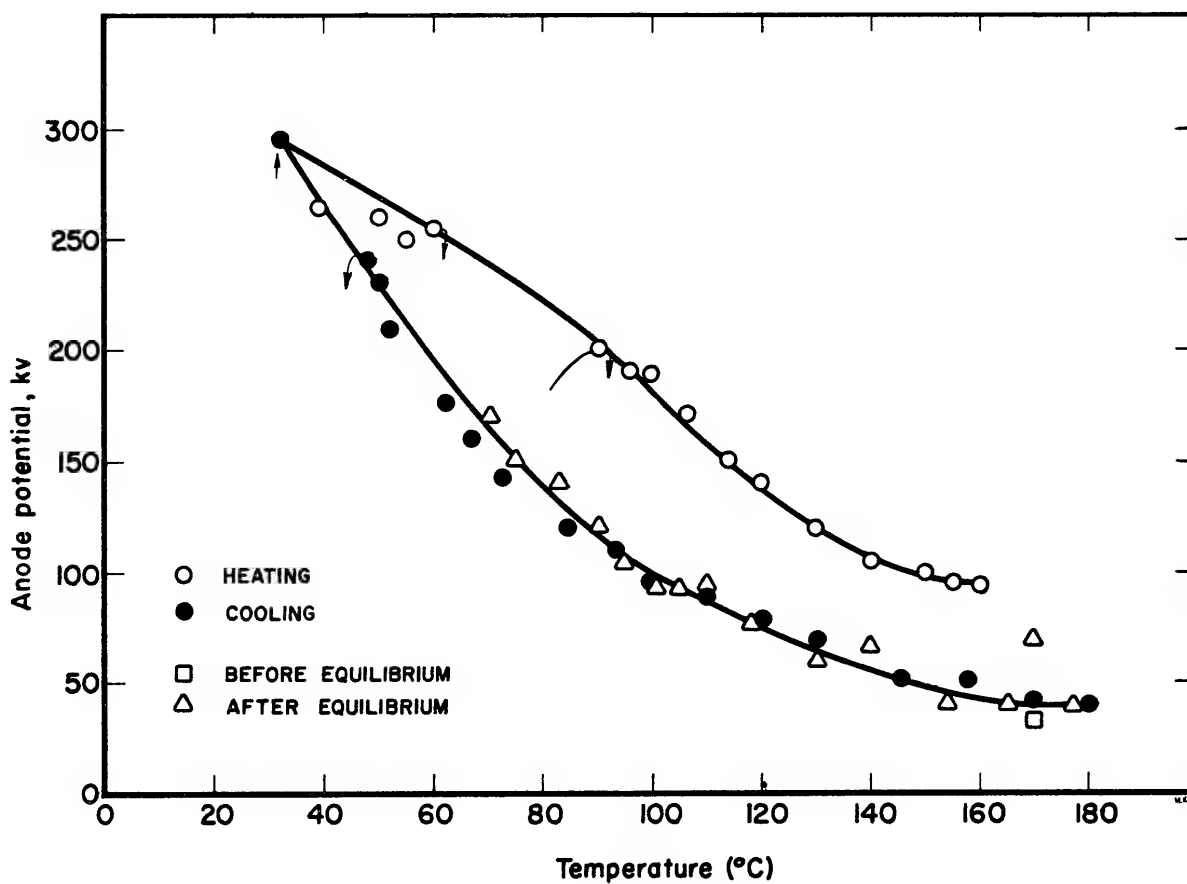
Fig. 8. Ambient Temperature Dependence

Fig. 9. Nonequilibrium Temperature Dependence

additional neat leak not present during the high-voltage experiments. Tem-
perature differences between anode and cathode at thermal equilibrium with
the thermocouple in place were then measured at a series of cathode tempera-
tures. These temperature differences (which ranged from 19°C at 200° to zero
at room temperature) were taken as a measure of the maximum error the thermo-
couple might introduce. In this way, limits were set on the anode temperatures.
The voltages attained are replotted in Fig.10 as a function of the anode
temperature.

The result of cooling the 1-liter spherical chamber to 0°C in an ice
bath, while at voltage and deliberately contaminated, is shown in Fig.11.
The two lower curves were taken in the presence of alumina saturated with
n-tetracosane in one case and with sulfur in the other. For the third curve,
a sample of alumina containing 47% of the saturation amount of sulfur was
used. Here, the experiment was continued by draining the ice bath and allowing
the chamber to return to room temperature. Under the conditions of the exper-
iments, the cathode wall reached the temperature of its surroundings shortly
after the outside temperature was changed, but several hours elapsed before
the anode approached within one degree of the same temperature.

Both the lower curves show initial voltage breakdown. This probably
resulted from jarring the apparatus while transferring it to the ice bath.
As a result, the voltage rose rapidly until the starting voltage was regained.
Thereafter, the adjustment to a new equilibrium voltage was quite slow. This
slowness in equilibration was also apparent during the temperature rise in
the experiment with the unsaturated sulfur sample.

DISCUSSION

The adsorption experiments indicate that contamination is indeed a fac-
tor in the dark current in that range of electrode fields and potential
differences where an exchange current flows. Since the maximum voltages
attained were found to be independent of the pressure of noncondensable gases
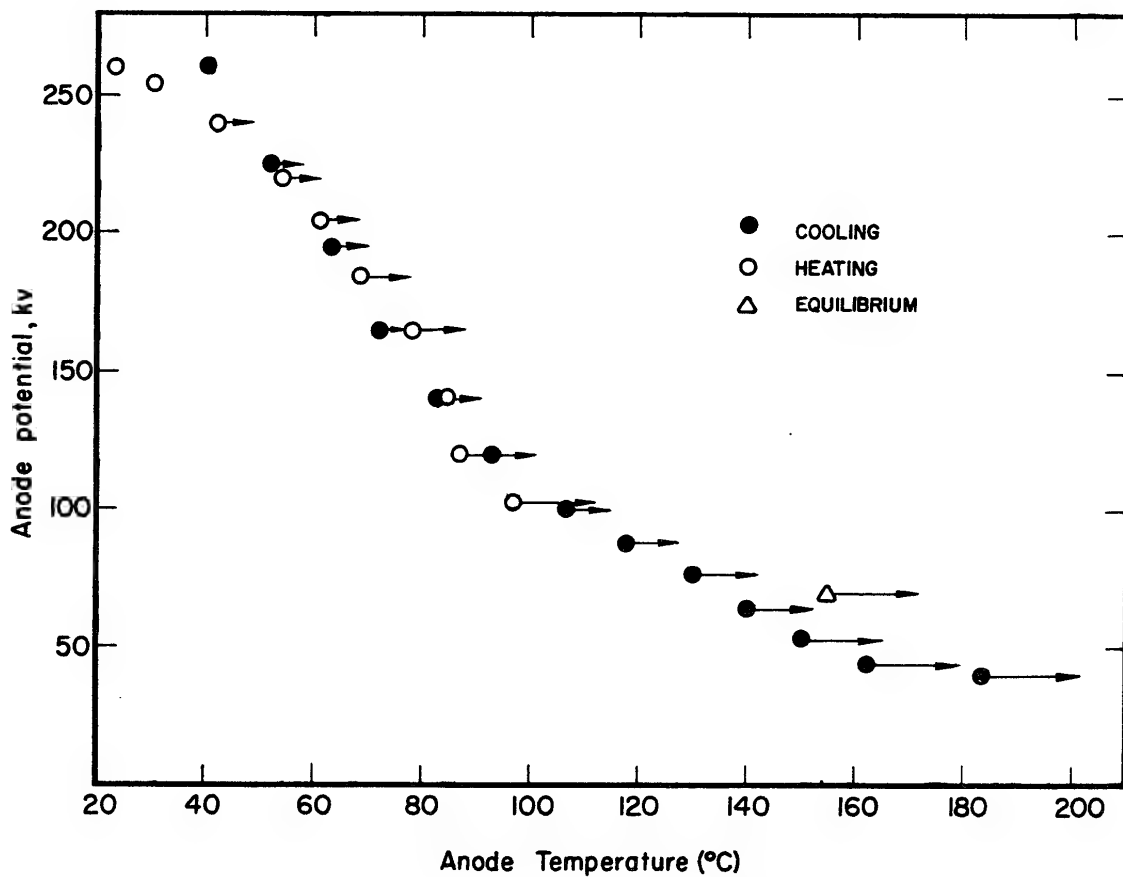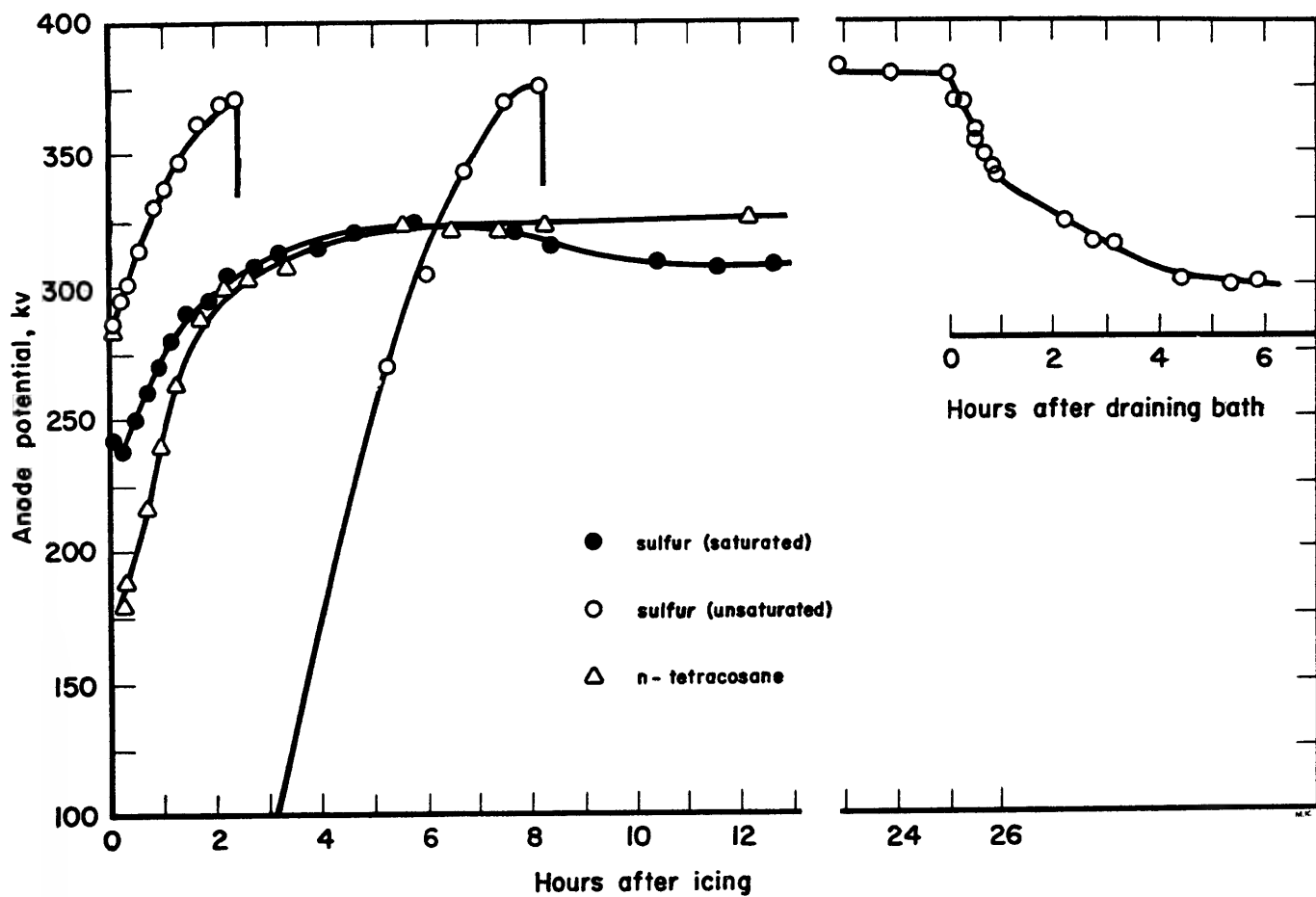
Fig. 10. Anode-Temperature Dependence

Fig.11. Temperature Dependence with Contamination

below a few times 10^{-4} mm of mercury, we may conclude that the effect observed
with these low-vapor-pressure contaminants was due to adsorption on the elec-
trodes. The temperature-dependence experiments further indicate that the
important adsorption occurred on the anode, since the system response to changes
in ambient temperature was quite slow and the voltage was found to follow the
anode temperature rather than the cathode temperature.

These experiments also indicate that the effectiveness of a contaminant
varies with the degree to which it covers the anode surface. In Table III are
tabulated the average layer thicknesses formed by various adsorbates at satura-
tion. The amount required to achieve saturation is taken from Fig. 7. The
alumina area is taken as 240 m^2/g, and the density of the normal form of the
contaminant at room temperature is used. If monomolecular adsorption is
assumed, the areas occupied per molecule are those given in the second column.
The numbers obtained for thickness and area per molecule are quite reasonable,
indicating that adsorption did indeed stop after about one monolayer of materi-
al had been deposited. The wide variation in the sizes of the sites occupied
suggests physical rather than chemical adsorption, a fact further indicated
by the ease with which adsorption and desorption were accomplished. When samples
containing less than the saturation amount of contaminant were exposed in the
chamber, the anode became covered with less than a monolayer of adsorbate,
but this amount was still sufficient to markedly affect the flow of the dark
current.

The effectiveness of a particular contaminant in promoting the dark
current appears to be directly related to its vapor pressure. In Fig. 12 the
voltages attained with alumina samples saturated with various contaminants
are shown as a function of the vapor pressures of the contaminants. (The
vapor pressures were obtained by extrapolation of published values obtained
at higher temperatures.) Since in all cases these steady voltages were
reached rather rapidly after the chamber was opened to the contaminant, it is

Table III

SATURATION THICKNESSES OF ADSORBATES

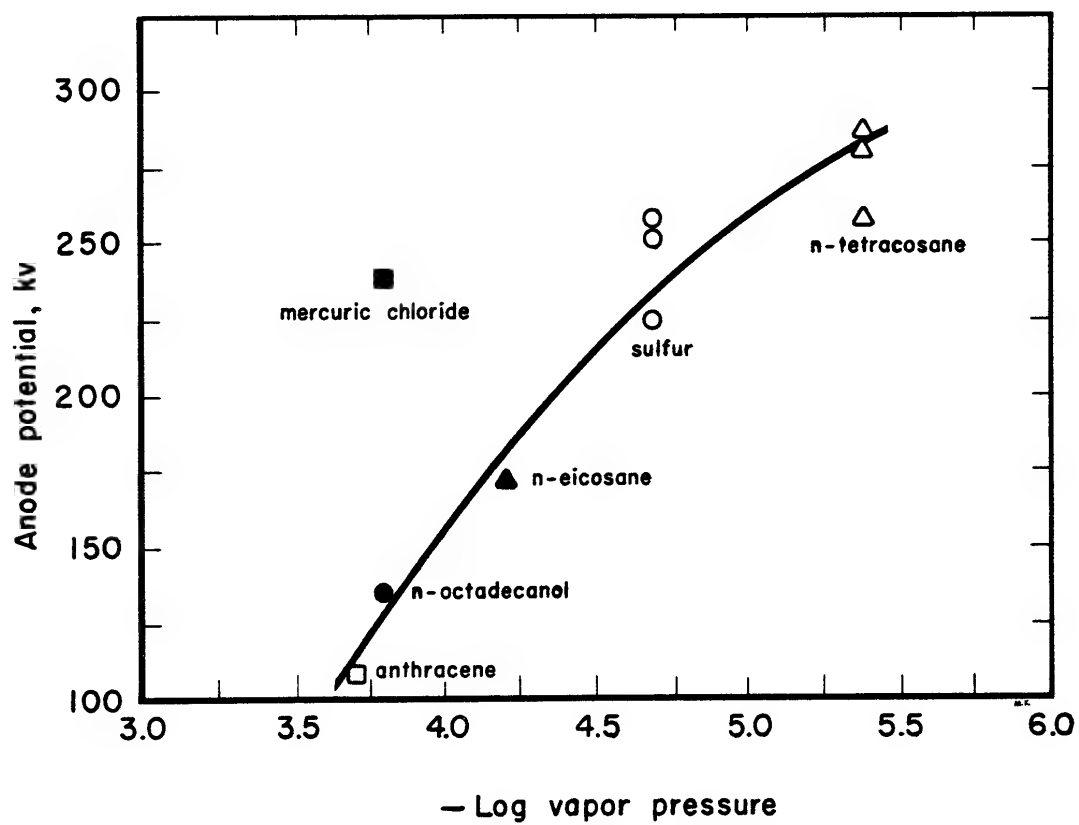| Adsorbate	Saturation thickness (A)	Area per molecule (A^2)
n-Tetracosane	6.9	104
Sulfur	6.2	21
Mercuric chloride	2.1	40
n-Eicosane	7.3	83
n-Octadecanol	9.6	58
Anthracene	4.8	49

Fig.12. Effect of Contaminant Vapor Pressure

apparent that the vapor pressure is not only important in the sense that it limits the diffusion of contaminant into the vacuum chamber, but also bears some direct relation to the part which the adsorbate plays in the dark-current mechanism.

If it is assumed that changing the temperature of the chamber affects the leakage current only through the vapor pressure of contaminants, then the data of Figs. 8 and 11 may be combined to give a vapor pressure--temperature relationship for an unknown contaminant still present in this thoroughly out-gassed system. Extrapolation of these vapor pressure data indicates that the contaminant has a residual vapor pressure in the neighborhood of 10^{-7} mm at room temperature. This is just the order of magnitude commonly measured by the ionization gauge in a "clean" system.

The anode adsorption experiments leave unanswered the question of whether the highest voltages attained in these experiments are limited by the same mechanism operative in a contaminated system, or by some new mechanism which becomes important under "clean" conditions. The temperature-dependence experiments indicate that the latter is the case. It will be noted that no further improvement in voltage is obtained by cooling a given system below some temperature where the voltage ceases to be temperature dependent, even though liquid nitrogen temperature is reached. In the 1-liter chamber with a 1-cm anode (the system in which the adsorption experiments were made), this transition temperature is just above room temperature. An extrapolation of the temperature-dependent part of the curve to 25°C indicates that a clean system could reach 500 kv if the vapor-pressure-dependent mechanism alone were operative. (This value agrees closely with the maximum voltage achieved in this work; i.e., approximately 535 kv attained with an 0.6-cm anode and 180-$\mu\mu$a source in a clean, 1-liter, spherical glass chamber.) It would appear

that in a system containing only residual contamination of sufficiently low vapor pressure, a dark current flows which is independent of this vapor pressure, but dependent on some other system parameters.

CONCLUSIONS

These experiments indicate that materials adsorbed on the anode surfaces in high-voltage generators can have a marked effect on the flow of the exchange dark current. The amount of adsorbate needed to produce a measurable effect is less than a monolayer, and the magnitude of the effect is apparently related to the vapor pressure of the material; i.e., the higher the vapor pressure of the adsorbate, the lower the voltage at which the exchange current sets in. The threshold voltage, with a given degree of contamination, decreases as the temperature, and therefore the contaminant vapor pressure, increases.

III--EFFECT OF THICK FILMS ON ELECTRODES

As a complement to the experiments described in Section II, a few
experiments were made in which larger amounts of less volatile contaminants
were placed on the anode and cathode surfaces. While the earlier work was
concerned with monolayers of contaminants with vapor pressures in the region
of 10^{-4} to 10^{-7}mm, the present work was concerned with visible amounts of
viscous greases. The experiments were performed in the 22-liter glass
spherical chamber described in Section I, using a 1-cm-diameter anode and a
72-$\mu\mu$a beta source. In most of this work, the contaminant was Apiezon N
grease, which was placed at points of interest in spots 2-5 mm^2 in area and
of irregular thickness. Repeated experiments showed that the presence of a
grease spot on the cathode did not affect the voltage limitation, but that
a similar spot on the anode did. In fact, even though most of the grease
in a new anode spot was quickly and spontaneously transferred to the cathode,
it was necessary to remove only the grease from the anode to regain high
voltage.

The effect of anode grease spots varied considerably in magnitude. During
this work the equilibrium system voltage without deliberate contamination ranged
from 120 to 215 kv. Placing a grease spot on the anode resulted in lowering the
voltage to between 60 and 120 kv. There was no apparent correlation between high
initial voltages and high final voltages.

The effect of the anode spots diminished with time after application, pre-
sumably because of the previously mentioned spontaneous transfer of grease from
anode to cathode. One such case is shown in Table IV. While most of the transfer
occurred during the first few hours after grease was applied, the rate of transfer
from the thin residual layer was still sufficiently rapid after a day or two of
operation for visible amounts to be deposited on a cleaned cathode surface in one
day's operation at high voltage. Rough measurements indicated that residual grease
layers on the order of 1μ thick effectively caused voltage reduction.

Table IV

TIME DEPENDENCE OF VOLTAGE REDUCTION

Age of anode spot (hrs)	Anode potential (kv)
not present	150
5	77
17	105
64	133

In many of these experiments a 2.5-cm-diameter aluminum disk was supported in the vacuum chamber near the cathode. This disk (the "collector") served as a part of the cathode but was electrically isolated from it through a micromicro-ammeter. The disk was shielded from the anode by a small grid in the same way that the entire cathode of our large cylindrical system was shielded in other experiments.

With the grease spot so oriented that all transferred grease struck the collector, only a small fraction (8-20 μμa of a total of 72 μμa) of the leakage current was drawn from the collector. In one such case the presence of the spot reduced the anode potential from 217 to 105 kv, even though the collector current was only 13 μμa, or 18%, of the total leakage current at equilibrium (i.e., 105 kv). In the absence of the spot, the leakage current from the entire cathode would have been negligible at this potential, but with the spot present, the remaining area apparently drew the other 82% of the current. When the grease spot on the anode was so oriented that grease did not strike the collector, the current drawn from this area was small, usually less than 1 μμa. (The collector represented only a very small fraction of the total cathode surface area, and drew similarly small currents when the system attained its equilibrium voltage in the absence of an anode spot.)

Application of a negative bias to the grid in front of the collector cut off the current from the collector. With the anode grease spot pointed toward the collector, biasing the grid turned off not only the collector current but also, apparently, the current from the other cathode areas as well, since the system voltage promptly rose to the value it had attained before the grease was introduced. With the anode spot pointing away from the collector, biasing the grid had no measurable effect on the limiting voltage.

It was noted in Section I that a blunt protrusion on the anode had no appreciable effect on the anode potential under ordinary conditions. This was not the case, however, when the anode spots were applied. In a typical experiment, the system gave 147 kv with a 1-cm-diameter anode equipped with a clean protruding rod of 2-mm-diameter with a polished, hemispherical end. A grease spot placed on the anode surface reduced the voltage to 112 kv; a similar spot on the end of the rod reduced the voltage to 45 kv, which was a lower value than any observed with the spot on the less sharply curved portion of the anode, with or without the protrusion.

The current drawn from the collector showed an unexpected decay phenomenon when the anode spot was rotated away while at equilibrium voltage. A few minutes after the anode was rotated so that instead of facing the collector the spot faced a point on the cathode 90° from the collector, the collector still drew some 15-20% of its maximum current. The anode voltage remained constant during the entire procedure.

Although Apiezon N grease was the only contaminant studied extensively in these experiments, tests of a few other nonvolatile materials indicated that harder substances, such as paraffin wax and Zapon lacquer, caused no voltage reduction from the highest potentials obtained in the system under discussion, i.e., 200-240 kv. All soft greases which were tried, including Myvacene-S (a silicone grease), Kel-F 40 (a fluorocarbon oil), and petroleum jelly, behaved in the same way as did Apiezon grease. Since visible amounts of grease were transferred at the very low currents available in these experiments, we conclude that charged particles containing many molecules came off the anode. It is not surprising that such particles are more easily extracted from a grease than from a hard wax or lacquer. These large particles apparently release enough secondaries

on striking the cathode to reinforce the otherwise non-self-sustaining chain between the anode and cathode and to cause an exchange current to flow between them. From the experiments in which a grid in front of the collector was used to control the entire leakage current, it is apparent that the coefficient product for the exchange current is a slow function of the voltage. (At the voltage attained with the collector cut off by a grid, the coefficient product must have been unity. At the voltage attained with the collector unprotected, about 100 kv lower, the coefficient product which served to multiply the spot--collector current was still about 0.9.) The experiments do not indicate whether the grease particles themselves were of primary or secondary origin.

IV--THE ROLE OF POSITIVE IONS

The first three sections of this report describe the results of experiments which indicate that positive ions frequently play an important part in vacuum conduction. In this paper we present experimental evidence concerning the specific nature and role of positive ions flowing across a vacuum space from anode to cathode.

EXPERIMENTS

The vacuum systems used in these experiments have been described earlier. The large, cylindrical brass system was provided with an electron multiplier structure[13] for positive-ion detection. This system will be termed the "dirty" system, since it was equipped with rubber gaskets and evacuated with an oil diffusion pump, and therefore all interior surfaces soon became coated with a "thick" film of pump oil. Another vacuum system, the "clean" system, was constructed entirely of Pyrex so that it could easily be cleaned and outgassed. This system was evacuated by a mercury diffusion pump and cold trap. A 1-liter spherical flask or any one of several cylinders were used interchangeably as the main vacuum chamber. This system was provided with a scintillation counter for the detection of positive ions. The detecting element consisted of a single-particle layer of ZnS-Ag, prepared by the method of Koller,[14] deposited directly on the face of a DuMont 6292 photomultiplier tube.

The mass-to-charge ratios of positive ions, which originated at the anode, were determined by measuring the deflection produced by a magnetic field perpendicular to the path of the ions. The energy-to-charge ratios of the positive ions were determined by measuring the deflection produced by an electric field perpendicular to the path. A schematic diagram of the arrangement for these measurements is shown in Fig. 13. Both the electric and magnetic fields were
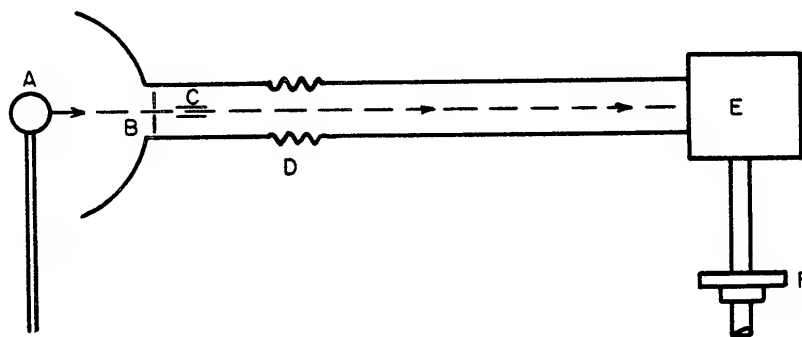
Fig.13 -Mass spectrometer. A, anode; B, beam-defining slit; C,
electrostatic deflection plates; D, silphon joint to allow
movement of E; E, ion detector; F, screw positioning de-
vice for E. The magnetic field is perpendicular to the
plane of the drawing and is located at point C.

calibrated using a sample of the alpha-emitter Po^{210} as a source of particles
with known mass, charge, and energy.

The number of secondary charged particles produced on the average by each
positive ion was measured in the large cylindrical system. The experimental
arrangement of Faraday cage, target, and counter is illustrated in Fig. 14.
Positive ions from the anode, A, passed through the grid, B, and struck the
target, D. A potential difference between the target and the collector, C,
allowed collection and measurement of the secondary currents of positive or
negative particles. A small, known fraction of the positive ions passed through
a slit, E, and were detected with an electron multiplier, F.

Observations of the production of positive ions by low-energy electrons were
made with the apparatus illustrated in Fig.15. This apparatus was attached to
the "dirty" vacuum system, and electrons from the tungsten filament, A, were
accelerated to the aluminum target, D, by a potential difference of 300 v.
The ions produced on the target were then detected with an electron multiplier,
F. The current of positive ions could be stopped by biasing grids B and C or
grid E. The current to the target was measured with an electronic electrometer.

<div align="center">RESULTS</div>

The results of these experiments are presented in three sections, the first
containing the results of experiments carried out in the large, brass, oil-pumped
system; the second, the results obtained in the Pyrex vacuum chambers; and the
third, results of experiments with low-energy electrons.

<div align="center">The Large Cylindrical System</div>

Positive ions were invariably emitted from the anode of this system at
limiting anode potentials. At an anode potential of less than the limiting value,

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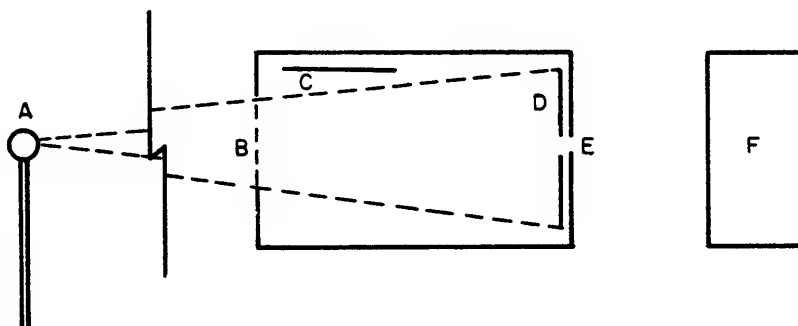Fig.14 -Experimental arrangement for measuring production of
secondary charged particles. A, anode; B, fine wire
grid; C, current collector; D, target; E, slit (to al-
low passage of a fraction of ions incident on target);
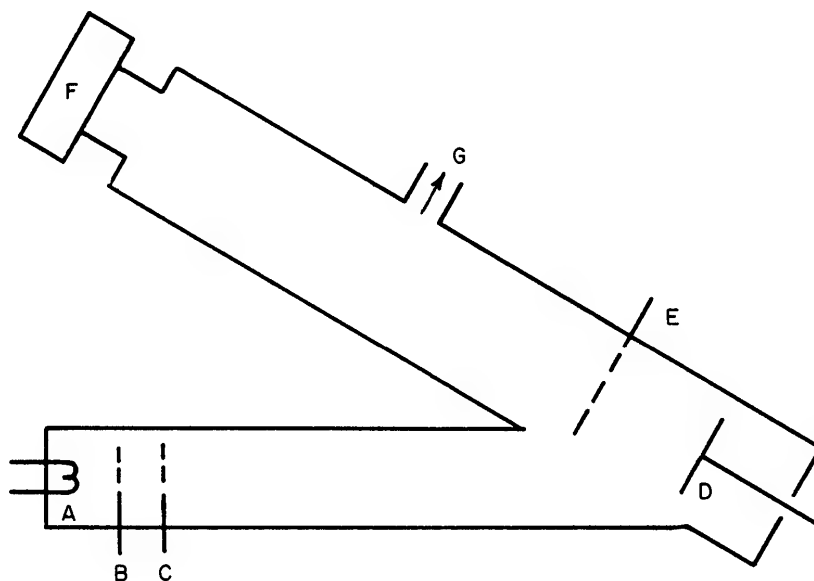F, ion detector.

Fig. 15 -Electron bombardment apparatus. A, tungsten filament; B,
C, E, fine wire grids; D, aluminum target; F, positive-
ion detector; G, opening to oil-pumped vacuum system.

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the particular circumstances determined whether or not a measurable number of positive ions were emitted.

The relation between positive-ion count rate and voltage is illustrated for several situations in Fig. 16. The curves illustrate the transition from one type of behavior to another. When a high negative bias (-1500 v) was used on grid 2 (the grid nearer the anode), the counting rate of positive ions increased as the anode potential increased, and reached a maximum steady value at the limiting anode potential. In the case of the 2.5-cm anode with a low bias on grid 2 (-300 v), the maximum count rate and limiting voltage occurred at a potential only slightly higher than that at which the positive ions were first observed. In the case of the 1-cm anode with a high bias on grid 2, the anode potential more than doubled after the positive ions first appeared in measurable numbers.

The sudden onset of leakage current observed with a low bias on grid 2 at an anode voltage close to the limiting value (curves A and B, Fig.16) is to be expected if the current is carried by a charge-exchange mechanism in which the secondary coefficients are only slightly current-sensitive. On the other hand, the appearance of a sizeable current at a potential much lower than the limiting value suggests that the mechanism is such that the current is directly dependent on the anode potential. One such process is the return of beta particles to the anode as a result of the anode field. We believe that the positive-ion currents in this oil-pumped system do arise in this manner. The sudden onset of current when there is a low bias on grid 2 is believed to be the result of the multi-plication of a beta-induced current by means of a charge-exchange process. A high bias on grid 2 prevents the return of a majority of the secondary negative particles from the cathode to the anode and thereby prevents the occurrence of an exchange-type current.
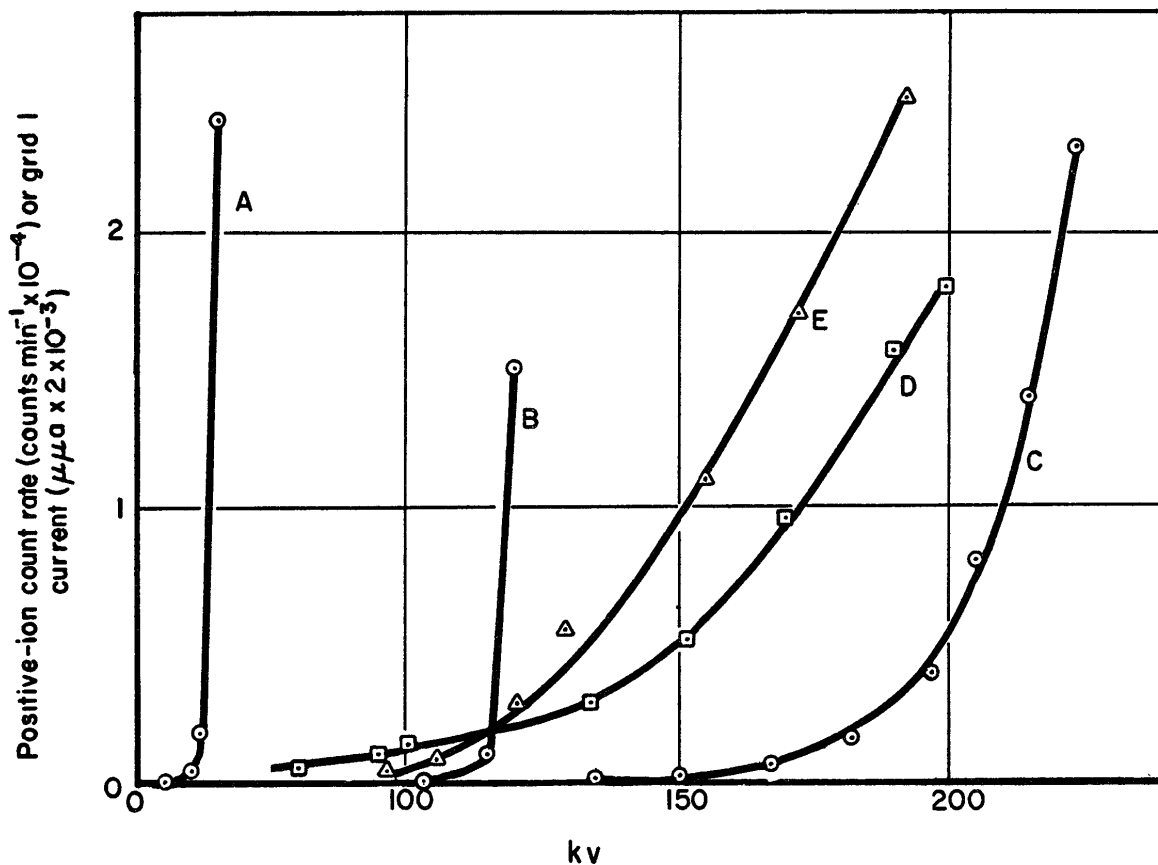
Fig.16 –Positive-ion emission as a function of anode potential. A, B, C, 2.5-cm anode
        with biases of 0, -300, and -900 v respectively on grid 2; D, emission from
        1-cm anode with -1500 v on grid 2; E, grid 1 current under conditions given for D.

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400 μμa of negative current when the anode contained a beta source which could provide a charging current of 35 μμa at that voltage (the current from a beta source is reduced to about 65% of its original value at 150 kv). Assuming that positive ions carry all this current and that the 400 μμa is three-fourths of the total secondary current (due to the screening fraction of one-fourth for grid 1), we find that the ratio of secondary negative to primary positive particles is 15. This ratio is certainly too small, since a finite fraction of the total leakage current to the anode must be carried by secondary negative particles produced at grid 2 by the positive ions which strike there.

The yield of secondary negative and positive particles was also measured with a Faraday cage in conjunction with the ion-detection device. The results of these experiments are illustrated in Fig.18. The values of the coefficients are based on the assumption that the electron multiplier counted the incident positive ions with 100% efficiency. An analysis of a pulse-height spectrum indicated that the counting efficiency was close to 100%. The value of 35 for brass with grease at 150-kv ion energy is to be associated with the coefficient 15 as obtained from grid currents. The actual value is probably closer to 35 than to 15.

The mass spectrometer was used to determine the apparent mass-to-charge composition of a beam of positive ions originating at the anode surface. These mass-to-charge ratios extended from less than 1 atomic mass unit per electronic charge to more than 2000 units. Table V presents the mass-to-charge ratios and intensities of peaks normally observed. We estimate that the values of the mass-to-charge ratios from mass-to-charge 27 to mass-to-charge 1.0 have an uncertainty of about ±15%. The uncertainty for mass-to-charge ratios of about 200 is ±30% and increases approximately as the square root of the mass above this value.

The relative intensities of the various species varied from day to day and had no apparent correlation with anode voltage, anode size, or grid bias.
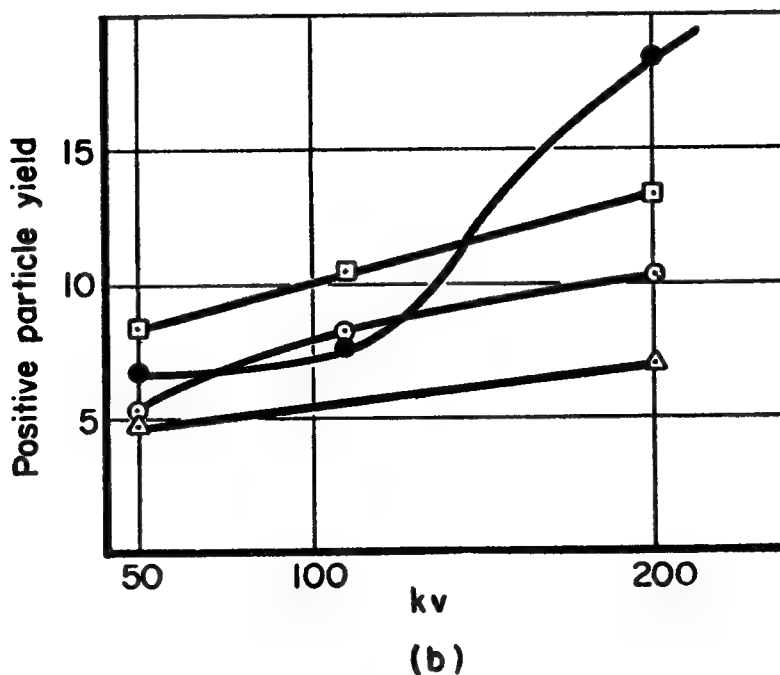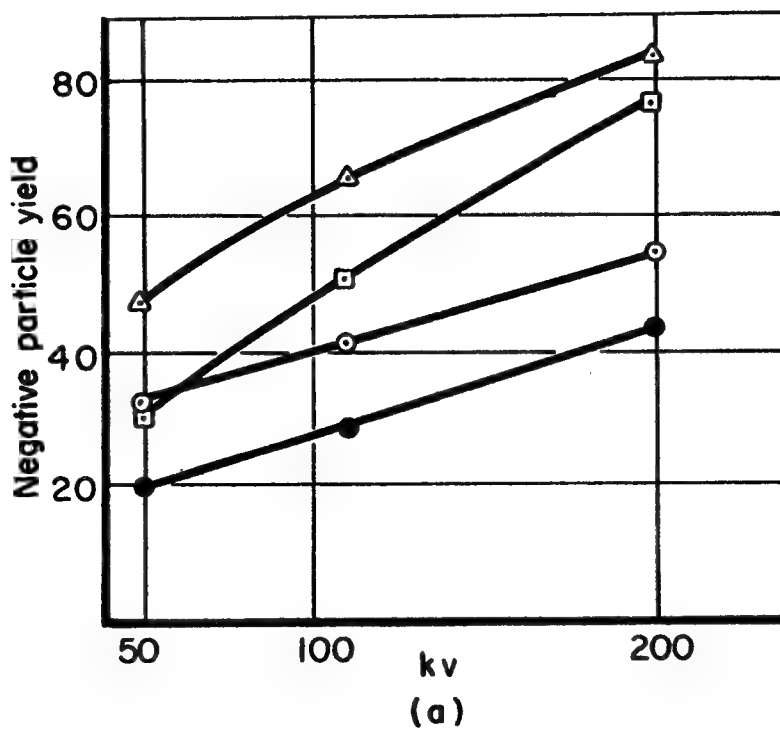
Fig. 18 -(a) Secondary negative particles per incident
positive ion. (b) Secondary positive particles
per incident positive ion. Target material:
⊙, brass; ▢, aluminum; △, lead; ●, brass
coated with grease.

Table **V**

Mass-to-charge ratio	Relative intensity		Mass-to-charge ratio	Relative intensity
0.65	13		83	65
1.0	35		101	41
1.4	13		121	52
1.64	3.5		160	70
2.0	4.4		215	35
8.8	4.4		244*	30
13 14 15	19		324*	43
27	105		425* 511*	35
32	105		895*	43
45.7	100		1627*	30
63.3	27		2395*	30
73.5	44		Infinite	87

*The intensity of these peaks varied from zero to the value noted. Where two or more numbers are combined and only one intensity appears, this intensity is the sum of the average intensities of the various peaks.

The peak at mass-to-charge infinity was composed of neutral particles, as shown by the failure of an electric field to change its position. These neutral particles must have resulted from decomposition of positively charged molecular ions in flight between the anode and the point at which they entered the magnetic or electric field. We believe that those ions with an apparent mass-to-charge ratio of less than one, and perhaps several other low-intensity peaks, are due to the positive-ion fragments which result from decomposition in flight. This suggests that decomposition may also occur on the anode surface if the time spent on the anode surface is of the order of or longer than the time of flight. The latter time is of the order of 10 μ sec for an average ion.

The Pyrex Vacuum System

A typical mass-to-charge analysis of positive ions which originate at the anode surface in this system is shown in Table VI. The experimental accuracy of the mass-to-charge ratios was limited primarily by momentary fluctuations in anode voltage and by the lack of high resolution of the deflected ion beam. This accuracy normally varied from $\pm 10\%$ for light ions to $\pm 25\%$ and $\pm 100\%$ respectively for ions with mass-to-charge ratios of 100 and 1000. These ions were normally detected at limiting voltage as long as there was no cathode grid with a negative "cutoff" bias. The scintillation counter apparently detected lighter ions more efficiently than heavier ions, presumably because of the greater penetration of the phosphor by the lighter ions. Because of this and because the ion detection devices differed in other physical details, the intensities of the various ion species in this system should not be compared directly with those in the "dirty" system

In Section I it was indicated that the anode potential could be increased from 100 kv to as much as 400 kv by "cleanup" of the vacuum chamber.

Table VI shows the effect on the ion spectra of baking the glass system for several days at $300^{\circ}C$. The peak at a mass-to-charge ratio of 2, the very heavy ion peaks, and the peak at infinite mass-to-charge ratio were not observed after cleanup. The position of the latter peak was not changed by an electric field and therefore the peak must be produced by energetic, uncharged molecules. The four light peaks (at mass-to-charge 1, 13, 28, and 42) were present in most experiments after cleanup.

A transfer of metal between electrodes at high potential in vacuum has been reported.[15] Experiments were performed in the "clean" system in order to determine whether the peaks at 13, 28, and 42 were produced by ions of aluminum (the usual anode material) or its oxides. Several anodes were prepared from titanium, from brass, and from molybdenum. Spectra were obtained with these anodes immediately after machining, again after polishing with iron oxide, and finally after polishing with aluminum oxide. In each case the anode was cleaned--with soap and water, with water alone, or with methanol. The spectrum from each anode was essentially identical to those obtained with an aluminum anode, and no new peaks appeared which could be related to the anode metal or metal oxides. It should be noted that our electrode current densities, less than 10^{-10} amp cm^{-2}, are much lower than those normally investigated. Different phenomena might therefore be expected at the electrodes.

We believe the positive ions originate in impurities adsorbed on the anode surface. A variety of substances were tested to determine whether or not they could act as sources of positive ions. A brief exposure to relatively high pressures of H_2, O_2, CO_2, or D_2O did not affect the anode voltage or the spectrum of positive ions in the "clean" system. In one series of experiments, samples of H_2, O_2, and CO_2 were each sealed in a glass ampule with 5 g of activated alumina. The ampule was then exposed to the vacuum chamber through a break-seal,

Table VI

Mass-to-charge ratio	Relative intensity	
	Before cleanup	After cleanup
1	83	66
2	58	--
2.3	58	--
13	42	33
28	100	100
42	66	28
60	42	--
155	20	--
300	41	--
2500	47	--
Infinite	40	--

with the entire system maintained at room temperature. The results of these ex-
periments were entirely negative; i.e., no changes occurred in anode voltage or
in the spectrum of positive ions. (In a completely different experiment, O_2 was
allowed to leak slowly into the "dirty" system. This seemed to produce erratic
changes which persisted for several days after the leak was stopped.) In another
experiment, one ml of D_2O was admitted to the "clean" system and a spectrum was
taken. No peak appeared at 2, 4, or 20.

Other possible contaminants include slightly volatile organic materials from
the fore-pump oil or from the atmospheric pollution normally found in metropolitan
areas.[16] In one case, a sample of n-eicosane ($n-C_{20}H_{42}$) was used to contaminate
the "clean" system. The anode voltage was reduced from 300 kv to 70 kv, a re-
duction considerably greater than that found by Merten[2] for this compound. It
seems likely that the n-eicosane itself was contaminated by a substance or sub-
stances with higher vapor pressure than that of n-eicosane. Spectra taken before
and after contamination are recorded in Table VII. The latter spectra do not
exhibit a measurable peak at 283, which would correspond to the n-eicosane molecule
ion. This is significant in that n-eicosane was present on the anode surface but
made no important contribution in the form of n-eicosane molecule ions. This may
be interpreted as an indication that ions formed on the anode surface undergo
chemical reactions such as decomposition or recombination before escaping by an
evaporative process. Those peaks which did appear or which increased in intensity
because of the presence of the contaminant may have been produced by fragments of
n-eicosane molecules or by molecule ions or fragments of other contaminants
introduced with the n-eicosane. A neutral peak, from ion decomposition in flight,
was also present.

The positions of the peaks in our spectra correspond roughly to the electron-
produced fragments obtained from normal paraffins in conventional mass spectro-

Table VII

Mass-to-charge ratio	Relative intensity	
	Clean	Contaminated
1	62	--
13	12	10
24	100	100
42	16	33
72	11	45
100	--	22
190	--	28
Infinite	--	27

meters. The largest peaks for our "clean" system, however, occur at 1 and 24, while in conventional spectrometers these are relatively small. The conditions for ion formation on our anode surfaces, as well as the apparent greater sensitivity of the detector for light ions, are certainly sufficiently different from conditions of a conventional spectrometer to account for the observed differences in ion abundances.

When a cathode grid at a high negative bias was employed in the cylindrical "clean" system, a current approximately equal to the charging current was drawn from the grid at the maximum steady voltage. Under these conditions we were unable to detect any positive-ion current from the equatorial plane of the anode. When the grid was maintained at the cathode potential, current flowed from anode to cathode and positive ions were detected at the rate of 1000 min^{-1}. These observations may be interpreted in either of two ways. One interpretation is that at high bias no positive ions are emitted from the anode. This would indicate that a majority of the positive ions produced in the "clean" system with no grid bias are produced by negative ions rather than by electrons, since at high grid bias a large current (equal to the charging current) of electrons produces no ions. The other interpretation is that at high grid bias the positive-ion emission is closely confined to some area of the anode other than that particular area at which the counter is looking. Experiments with phosphors on the anode showed that in every case there was considerably more activity in the neighborhood of the supporting rod than in any other area of the anode. There is also strong evidence of a large degree of anisotropy in positive-ion emission from the anodes in the "dirty" system, especially at high grid bias.

Transient Effects in Positive-Ion Emission

Experimental observations in the "dirty" system suggested that the positively charged molecular ions escape from the anode surface by a mechanism resembling

evaporation. In order to determine whether or not this actually occurs in the "dirty" system, we counted the positive ions appearing in the first few milliseconds after the bias on grid 2 was suddenly increased. We found that the positive-ion current required about 1 ms to adjust to a new lower value. This lower value was identical to the value obtained at the same potential and grid bias under normal circumstances. Unfortunately, this does not prove beyond question that there is a delay in positive-ion emission. Calculations showed that this result might be explained by an alternative mechanism involving the decay of a charge-exchange current, with the flight time of the negative ions determining the characteristic time of the process.

In order to avoid this complication, we carried out similar experiments in which we bombarded a metal disk with electrons and observed the positive ions which were emitted as a result of this bombardment. The apparatus used is shown in Fig.15. We found that positive ions continued to flow from the disk to the counter for about 500 μsec after the bombarding current was turned off. This time was not associated with the flight time of the positive ions, since biasing a grid directly between the disk and the counter stopped the positive-ion current in less than 10 μsec. We conclude, therefore, that the delay observed in the "dirty" system is to be associated with evaporation of positive ions.

Measurements of the variation of the coefficient for positive-ion production with electron intensity were made. We found that this coefficient was essentially constant from 0.2 $\mu\mu$a cm^{-2} to more than 1000 $\mu\mu$a cm^{-2}. This is not consistent with the square-root law found for the production of ions by electrons on the anode. The conditions under which the two measurements were performed, however, were sufficiently different that this inconsistency is not surprising.

SUMMARY

We have shown that positive ions are usually a part of leakage currents occurring in our vacuum systems. The similarity of spectra obtained in a system deliberately contaminated with an organic substance to spectra obtained in a similar system before outgassing suggests that these ions originate in a film of organic material which is present to some degree on even the cleanest surface. There is evidence that these ions are formed by energetic negative ions or (in the case of very thick organic films) by electrons. There is also evidence that positive ions which are formed in thick anode films by the impact of electrons do not escape from the surface immediately, but rather escape by some process resembling evaporation. These ions are apparently subject to various decomposition and recombination processes while on the anode surface.

FOOTNOTES

[1] W. Schottky, Physik, Z. <u>15</u>, 872 (1914); E. L. Murphy and R. H. Good, Jr., Phys. Rev. <u>102</u>, 1464 (1956); M. J. Morant, Proc. Phys. Soc. (London) <u>B68</u>, 513 (1955).

[2] John G. Trump and R. J. van de Graaff, J. Appl. Physics <u>18</u>, 327 (1947); L. C. van Atta, R. J. van de Graaff, and H. A. Barton, Phys. Rev. <u>43</u>, 158 (1933); J. L. McKibben and K. Boyer, Phys. Rev. <u>82</u>, 315 (1951); C. M. Turner and J. P. Blewett, Phys. Rev. <u>81</u>, 305 (1951).

[3] R. J. Strutt, Phil. Mag. VI, 588 (1903); H. G. J. Moseley, Proc. Roy. Soc. (London) <u>A88</u>, 471 (1913); E. G. Linder, Phys. Rev. <u>71</u>, 129 (1947); E. G. Linder and S. M. Christian, Phys. Rev. <u>83</u>, 233(A)(1951) and J. Applied Phys. 23, 1213 (1952); P. Y. Feng and J. W. Kennedy, J. Am. Chem. Soc. <u>77</u>, 847 (1955).

[4] H. A. Bethe, Rev. Mod. Phys. <u>22</u>, 213 (1950).

[5] Moseley, <u>loc</u>. <u>cit</u>., and Linder and Christian, <u>loc</u>. <u>cit</u>.

[6] If $\underline{a}$ is the radius of the anode, and $\underline{b}$ the radius of the surrounding cathode, and $\underline{V}$ the potential difference, the fields at anode and at cathode in spherical geometry are given by:

$$\underline{E}_{\underline{a}} = \frac{\underline{V}}{\underline{a} - \frac{\underline{a}^2}{\underline{b}}} \quad ; \qquad \underline{E}_{\underline{b}} = \frac{\underline{V}}{\frac{\underline{b}^2}{\underline{a}} - \underline{b}}$$

For cylindrical geometry the relations are:

$$\underline{E}_{\underline{a}} = \frac{\underline{V}}{\underline{a} \ln\frac{\underline{b}}{\underline{a}}} \quad ; \qquad \underline{E}_{\underline{b}} = \frac{\underline{V}}{\underline{b} \ln\frac{\underline{b}}{\underline{a}}}$$

[7] W. Schottky, Z. Physik <u>14</u>, 63 (1923), analyzed the effect of sub-microscopic surface irregularities by considering bumps on top of bumps on top of bumps, etc. His conclusion was that the electric field intensity could in this way be increased by a factor of about ten. His derivation contains a gross algebraic error, without which the result would have been a factor of $2^{10} = 1000$. However, Schottky assumed successive bumps differing progressively in size by twofold, whereas tenfold probably ought to have been assumed. With these corrections we estimate field multiplication at microscopic surface irregularities by a factor of about $2^3 \approx 10$. For surfaces not highly polished we take this factor to be perhaps as high as 20.

[8] J. G. Trump and R. J. van de Graaff, J. Appl. Phys. 18, 327 (1947), and E. W. Webster, R. J. van de Graaff, and J. G. Trump, J. Appl. Phys. 23, 264, (1953).

[9] C. M. Turner, Phys. Rev. 81, 305 (1951).

[10] J. L. McKibben and K. Boyer, Phys. Rev. 82, 315 (1951).

[11] V. M. Stowe, J. Phys. Chem. 56, 484 (1952).

[12] S. Brunauer, The Adsorption of Gases and Vapors (Princeton University Press, Princeton, N.J., 1943), p. 287-8.

[13] J. S. Allen, Rev. Sci. Instr. 18, 7 9 (1947).

[14] L. Koller, J. Opt. Soc. Am. 43, 620 (1953).

[15] P. F. Browne, Proc. Phys. Soc. 68, 364 (1955).

[16] J. Trillat and H. Motz, Trans. Farad. Soc. 31, 1127 (1935).

SOME EXPERIMENTS ON ELECTRICAL CONDUCTION IN VACUUM

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